

THE REACTIVITY OF AMINES IN DEAMINATION REACTION ON ALUMINA

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The rates of deamination of a series of primary, secondary and tertiary amines on alumina were determined by the method of initial reaction rates. In addition quantum chemical calculations for the same series of amines were performed by semiempirical CNDO/2 method, the interaction of molecule with surface acid centre of the catalyst being modelled by protonation of the amino group. It was found that experimental reactivities correlate well with calculated properties of the C—N bond. This shows that the cleavage of this bond takes place in the rate determining step of the reaction, giving evidence for E1 elimination mechanism. The good correlation of the experimental with calculated data confirms the correctness of the concept of the molecular adsorption of the amine on the acid catalytic centre as the first phase of heterogeneously catalysed deamination reaction.

Till now, heterogeneously catalysed transformations of amines on nonmetallic catalysts have not been much studied. The first study was published by Brey and Cobblestick¹, dealing with decomposition of butylamines on alumina. The reactivity of a series of primary, secondary and tertiary amines on alumina was determined by Catry and Jungers². The kinetics of deamination was reported by Pašek and coworkers³⁻⁶ and by Lycourghiotis and coworkers⁷. Andréu and coworkers⁸ compared the reactivity of butylamines, butyl halides, and butanols on sulphates and for the given type of catalysts they found a considerable similarity in the composition of primary products of deamination, dehydrohalogenation and dehydration⁹. Several works¹⁰⁻¹³ concerned with the formation of diphenylamine from aniline on alumina.

By contrast to the chemical reaction as such, the adsorption of amines was studied in detail, being basis for the frequently applied method for determining the acidity of surfaces of solid compounds. The study of adsorption of amines and ammonia on alumina showed that strongly acidic Lewis centres that are present on the surface¹⁴⁻¹⁷ (Al ions) can be converted into weaker acidic Brønsted centres by water adsorption¹⁸⁻²².

The gas phase basicities of a series of amines were determined by Aue and coworkers²³. Theoretical calculations reproducing satisfactorily the basicities of a rather narrow set of amines were performed by Hehre and Pople²⁴ with the use of semiempirical CNDO quantum chemical method. The same method was used by Sedláček²⁵ to model the effect of different types of adsorption on the molecule of amino-, halogeno-, hydroxy-, and mercaptopropanes.

On alumina, the amines can undergo several types of adsorption, which leads to different transformations of amines²⁵⁻²⁸. This explains the fact that besides deamination the alumina

catalyses also disproportionation² and dehydrogenation of amines¹. The important role in the reaction mechanism of deamination is obviously played by surface hydroxyl groups of alumina that act as relatively weak acidic Brønsted centres. This is demonstrated by the fact that the deamination activity of the catalysts depends on temperature and on the pretreatment of the catalyst¹. It was found that an increase in temperature, which leads to dehydration (or more accurately to dehydroxylation), causes the decrease in the catalytic activity. The mentioned effect of temperature can be compensated to a large extent by introducing water vapour¹.

Of the great importance is also the fact that heterogeneously catalysed deamination is very closely related to other elimination reactions taking place on polar catalysts, *i.e.* to dehydrohalogenation, dehydrosulphidation and dehydration. Especially the last reaction has been the subject of detailed experimental studies^{8,9,29}. In seeking for hypotheses that account for regularities in the behaviour of amines, some concepts resulting from studies on dehydration of alcohols can be utilized with advantage.

The present work is concerned with deamination on alumina, the main goal being theoretical interpretation of experimental reactivities of a set of twenty two primary, secondary, and tertiary amines. Theoretical analysis was based on the simple and already tested model of adsorption^{2,5}. Quantum chemical calculations were made by using the well-tried semiempirical CNDO/2 method.

EXPERIMENTAL

Alumina used as the catalyst was prepared by precipitation of aluminium nitrate (per analysis) and ammonia (per analysis) solutions. The precipitate was thoroughly washed and then dried at 393 K for 24 h. After grinding, the fraction 0.2–0.4 mm was sieved and then heated to 723 K for 24 h. The specific surface of the so obtained alumina was 189 m²/g (determined by BET method).

Amines. Some of the amines were commercial preparations: diethyl- (Apolda-Chemie; impurities 0.01%), triethyl- (Sojuzkhimexport; 0.05%), dimethyl- (0.3%), propyl- (0.1%), ethyl (Fluka; 0.8%), butyl (0.2%), sec-butyl- (0.2%), isobutyl- (Koch-Light; 0.3%), isopropyl- (MCHZ Ostrava; 0.01%), methyl- (1%), and tert-butylamine (unknown producer; 0.2%). Most secondary and tertiary amines were synthesized by alkylation with alkyl halides. Diisopropylamine was prepared by hydrogenative amination of dimethyl ketone on Pd catalyst (400 K, 5 MPa). The purity of prepared amines was around 99–95%.

Reaction rate of deamination was measured by the method of initial reaction rates in a differential reactor on one pass. The amines were fed to a stream of carrier gas (nitrogen) with the use of a linear feeding device. The upper part of the reactor filled with crushed quartz served as the evaporator. The quartz tube reactor (15 mm i.d., 700 mm long) was placed in an electrically heated mantle and contained from 1.25 to 5 cm³ of the catalyst. The temperature measured with a Fe–Ko thermocouple that was placed in a coaxial quartz probe (3 mm e.d., 0.5 mm thick) was controlled with the accuracy of ± 0.3 K. Catalytic measurements were carried out at the partial pressure of amine equaling to 0.01 MPa and at two temperatures, 555 and 590 K. Reaction products were analysed by gas chromatography on two columns, using a flame-ionisation detector. The first column worked at the higher temperature and was used to analyse the whole reaction mixture with the aim to determine amines quantitatively. After separation of the amines by washing or by freezing, the remaining olefins were analysed on the second column at the lower temperature. The catalyst was regenerated after each 2–10 h of its performance, using a stream of air saturated with water vapour at laboratory temperature (723 K, 2 h) and was activated in a stream of dry nitrogen (723 K, 1 h).

QUANTUM CHEMICAL CALCULATIONS

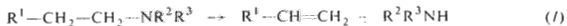
For the purposes of interpretation of reactivities of amines, the calculations were made by semiempirical CNDO/2 quantum chemical method, using the programme published in the book by Pople and Beveridge³⁰. Molecules of amines were constructed by using standard bond lengths³¹, tetrahedral bond angles and staggered conformations along all the bonds. Within the framework of these rules for construction of model systems, there exist several configurations (especially for greater molecules) that differ from each other in energetical suitability. For that reason, the calculations were always carried out for several possible configurations of a given system. For purposes of interpretation of the experiment, the results corresponding to the most stable configuration were chosen.

In modelling adsorption, the extent of activation of the molecule was judged on the basis of the following quantum chemical quantities: charge on atom N and H_A (H_A designates the hydrogen bonded to β carbon such that C_γ-N and C_β-H_A bonds be mutually antiperiplanar), the strength of C_γ-N and C_β-H_A bonds that was evaluated from Wiberg bond index³² and index FED (Frontier Electron Density) for LUMO on atom H_A (the index FED is the measure of the ability of a given atom in the molecule to be attacked by a basic agent).

The adsorption of amine on the surface acidic centre was modelled by protonation of the amino group. The importance of molecular adsorption to form the passive hydrogen bridge (R¹R²R³N⁺⋯H-O_{surf}; R¹, R², R³ = H or alkyl) as the initial stage of elimination reaction is documented by two facts. The first one is the experimentally found dependence of the deamination activity of the catalyst on the number of hydroxyl groups present on surface¹ (this dependence was verified also in the present work — see Results and Discussion) and the second is the result of quantum chemical calculations. The earlier calculations^{2,5} showed that interaction with the electron acceptor that withdraws electrons from amine molecule activates the molecule toward deamination. On the other hand, the increase in the electron density of the molecule, which is typical for dissociative adsorption on surface Al ion (R¹R²N⁽⁻⁾⋯Al_{surf}) activates the molecule toward dehydrogenation^{2,5}.

RESULTS AND DISCUSSION

It was found that under given conditions the amines undergo predominantly deamination on alumina, *i.e.* they give the olefin and the lower substituted amine, eventually ammonia.



Reaction products of primary and especially secondary amines contained a certain, usually relatively small amount of the higher N-substituted amines that were formed by disproportionation reactions.



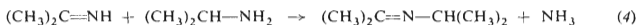
In the case of tertiary amines, the above mentioned disproportionation cannot proceed as the primary reaction step. Diethylamine yielded comparable amounts of

deamination and disproportionation products. This compound was therefore used to study the effect of the pretreatment of the catalyst on the rate of these two reactions.

These measurements have proved that the disproportionation activity of the catalyst is not affected when air used to its washing is saturated with water vapour (at ambient temperature). Contrarily, the same modification of treatment conditions – *i.e.* the substitution of procedure *A* (dry air, 1 h, 553 K; dry air, 2 h, 723 K; dry nitrogen, 1 h, 723 K) for procedure *B* (moist air, 2 h, 723 K; dry nitrogen, 2 h, 723 K) results in threefold increase in the deamination activity of the catalyst. It is of interest that nearly the same effect is obtained by the substitution of procedure *A* for procedure *C* (dry air, 1 h, 723 K – attained after 15 min; dry nitrogen, 1 h, 723 K) that – in comparison with procedure *A* – is characterized by the time interval at temperatures below 723 K as short as possible.

The observed behaviour of alumina corresponds to the concept that water which increases the catalytic activity in the direction of deamination, is adsorbed on the surface in an activated form, *i.e. via* dissociative adsorption taking place at increased temperature. On fast establishing the temperatures at which the activated adsorption can take place, the adsorbed water molecule cannot desorb and its dissociation leads to formation of catalytically active surface hydroxyls. If temperature is raised slowly, the adsorbed water molecule is removed from the surface³³ and is no thus available at the temperature ensuring its dissociation. This explanation is supported also by the fact that an analogous situation observed in dehydration of alcohols on alumina^{26–28} could be well described by Monte-Carlo model of dehydroxylation of alumina surface³⁴.

In the series of the amines studied, isopropylamine was found to exhibit different behaviour in the course of the reaction. In this case, the dependence of conversion on reciprocal space velocity was not linear even at very low conversions. Furthermore, besides propene also *N*-isopropylideneisopropylamine was found to be present among reaction products. A similar behaviour was observed also for cyclohexylamine⁵. With regard to the similarity in the structure of isopropyl- and cyclohexylamine (symmetrical branching on α carbon), one can assume that deamination of isopropylamine proceeds *via* cyclic mechanism that was proposed for the decomposition of cyclohexylamine⁵:



The attempt to detect isopropylideneimine in the reaction products has not been successful, which speaks for the high reactivity of this intermediate product. At the

same time, N-isopropylideneisopropylamine is not formed by dehydrogenation of the disproportionation product, diisopropylamine, since N-isopropylideneisopropylamine has not been found among reaction products arising from this amine. Furthermore, the reaction products formed from isopropylamine do not contain the product of disproportionation as such, *i.e.* diisopropylamine. Attempt to identify analogical N-n-alkylidene-n-alkylamines in the deamination of primary alkylamines was unsuccessful. Therefore, one can assume that the mechanism of deamination of isopropylamine or of cyclohexylamine and n-alkylamines is not identical.

Deamination rates determined for all the amines studied are given in Table 1.

Quantum chemical calculations by CNDO/2 method were made not only for all the amines studied experimentally in this work but also for the amines that were

TABLE I
Rates of deamination of primary, secondary, and tertiary amines (in mol dm⁻³ h⁻¹)

Amine	Olefin	$r \cdot 10^4$	
		555 K	590 K
Ethyl-	ethylene	6.03	97.7
Propyl-	propene	4.17	50.1
Isopropyl-	propene	70.8	1 150
Butyl-	butene	6.03	45.7
Tert-butyl-	isobutene	1 020	4 170
Diethyl-	ethylene	36.4	317
N-Ethylbutyl-	ethylene	11.7	97.7
	butene	57.5	501
N-Methylisopropyl-	propene	85.1	832
	ethylene	15.5	105
N-Ethylisopropyl-	propene	170	759
	propene	551	1 870
Diisopropyl-	propene	170	759
N-Isopropylbutyl-	butene	19.1	107
	ethylene	352	1 370
Triethyl-	ethylene	33.1	110
	propene	47.1	138
	butene	52.5	174
	ethylene	158	575
N,N-Dimethylethyl-	propene	120	537
	propene	479	1 740
N,N-Dimethylpropyl-	butene	107	525
N,N-Dimethylisopropyl-			
N,N-Dimethylbutyl-			

studied by Catry and Jungers². The good applicability of this method for description of the behaviour of amines is documented in Fig. 1. The figure demonstrates the excellent linear correlation of the basicities of the amines measured in gas phase^{2,3} with the energies of protonation of amines obtained by CNDO/2 calculation. The high correlation coefficient (0.99) confirms that semiempirical CNDO/2 quantum chemical method is able to describe the properties and behaviour of primary, secondary, and tertiary amines.

Based on what is known about the mechanism of deamination reaction and, to a large extent, also on analogies found in the study of the relatively well investigated mechanism of dehydration, one can presume that the deamination on alumina proceeds with participation of the pair of the acidic and basic surface centre²⁹. It seems likely that the initial stage of the reaction is molecular adsorption of the amine on the acidic centre, this being probably the surface hydroxyl group. With regard to the fact that amines do not usually form the structures analogous to surface alkoxides¹⁴⁻²² on alumina surface, they do not undergo obviously such an easy dissociation as do alcohols. For that reason, also alumina ion could play a role of the acid centre in the deamination.

In further phase of the reaction the molecule activated by adsorption²⁵ decomposes with participation of the basic centre – most likely of the oxygen ion – that interacts with the hydrogen bonded to the β carbon. This transformation is depicted by Scheme 1. Calculations proved that the most strongly activated β hydrogen is that located in antiperiplanar position with respect to the amino group²⁵ (designated as H_A in the present work). It is again worthy of note that this phenomenon has an analogy in the behaviour of alcohols²⁵, in which case it is demonstrated by the significant stereoselectivity of the reaction which proceeds as the anti-elimination.

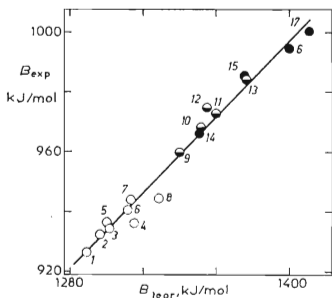


FIG. 1

Correlation of experimental basicities of amines measured in gas phase^{2,3} with theoretical basicities obtained from quantum chemical calculations. The basicity is defined as the change in enthalpy accompanying the reaction $R^1R^2R^3NH^+ \rightarrow R^1R^2R^3N + H^+$. \circ Primary amines, \bullet secondary amines, \ominus tertiary amines; 1 ethyl-, 2 propyl-, 3 butyl-, 4 isopropyl-, 5 isobutyl-, 6 sec-butyl-, 7 cyclohexyl-, 8 tert-butyl-, 9 diethyl-, 10 dipropyl-, 11 dibutyl-, 12 diisobutyl-, 13 di-sec-butyl-, 14 dimethylethyl-, 15 triethyl-, 16 tripropyl-, 17 tributylamine



SCHEME I

One can therefore assume that as far as the dependence on the rate determining step of the reaction is concerned, the experimentally found trend in the reactivity of the series of amines can be correlated with some of theoretical quantities that characterize the properties of the $C_\alpha-N$ or $C_\beta-N$ bond. Hence, for purposes of correlations with experimental data in the present work we have chosen ten quantities relating to the free amine molecule: *a*) the strength of the $C_\alpha-N$ bond, *b*) charge on atom N, and *c*) the strength of the $C_\beta-H_A$ bond, and further the quantities that relate to the molecule of amine on which the adsorption is modelled by protonation: *d*) the strength of the $C_\alpha-N$ bond, *e*) the relative change in the strength of the $C_\alpha-N$ bond due to adsorption, *f*) the strength of the $C_\beta-H_A$ bond, *g*) the relative change in the strength of the $C_\beta-H_A$ bond due to adsorption, *h*) charge on atom H_A , *i*) the absolute change in charge on atom H_A due to adsorption, and finally *j*) index FED in LUMO on atom H_A which is the measure of the ability of this atom to be attacked by a base.

The values of correlation coefficients of the linear correlations of experimental reactivities (logarithms of the reaction rate or logarithms of the rate constants) of the amines are summarized in Table II. As shown in Figs 2–4 on example of the correlation of reactivities and changes in the strength of the $C_\alpha-N$ bond, these correlations are successful only for the group of amines of the same type, *i.e.* primary, secondary, and tertiary amines. The reason for this fact can be found in that the reactivity of a given amine in deamination is estimated from the properties of the initial stage of the reaction, *i.e.* from adsorption of the molecule. With increasing number of substituents on nitrogen, the effect of the interaction modelling adsorption becomes less directed and divides into greater number of directions. The magnitude of the response of the interaction which remains constant in strength, is thus naturally decreased in going from primary to secondary and to tertiary amines. One can thus assume that the more accurate model, *e.g.* the model of activated complex of the surface reaction, would make it possible to describe the behaviour of all the amines by one correlation.

As follows from data presented in Table II, none of the quantities that characterize the properties of the $C_\beta-H_A$ bond (*i.e.* $-W(C_\beta-H_A)$ in the free and adsorbed molecule, $-\Delta W(C_\beta-H_A)$, $Q(H_A)$, $\Delta Q(H_A)$, and FED) correlate significantly with experimental data. Correlation of these quantities yields frequently even negative correlation

coefficients, which manifests contradictory trends in experimental and calculated values. Thus, for example, the theoretical measure of activation of the $C_{\beta}-H_A$ bond decreases in the series of primary amines, whereas the reactivity measured at both 555 and 590 K increases.

On the other hand, the quantities characterizing the properties of the $C_{\alpha}-N$ bond correlate with experimental data very well (see Table I and Figs 2 and 3), the positive signs of these correlations document their physical meaning. The fact that the rate of deamination on alumina is connected with the properties of the $C_{\alpha}-N$ bond proves that the rate determining step of the reaction involves most likely the cleavage of the $C_{\alpha}-N$ bond. This corresponds to the mechanism designated as E1 elimination²⁹. It is of interest that very good correlations are obtained not only with the quantities related to adsorbed molecule but also with the quantities that relate to the free molecule. This means that deamination reactivity of amine can be reliably estimated already from static properties of the isolated molecule.

One can find easily the rational physical interpretation of the obtained relationships between experimental and theoretical quantities: a) The ease of deamination depends on the strength of the $C_{\alpha}-N$ bond in amines. It holds not only that the less strong bond, the easier its cleavage but obviously also that the weaker bond, the stronger

TABLE II

Coefficients of linear correlations of experimental deamination reactivities ($\log r$, $\log k$) with selected calculated quantum chemical quantities

Quantity ^a	555 K			590 K			Catry, Jungers ²		
	prim.	sec.	tert.	prim.	sec.	tert.	prim.	sec.	tert.
$-W(C_{\alpha}-N)^b$	0.99	0.86	0.85	0.99	0.86	0.81	0.68	0.97	-0.88
$-Q(N)^b$	0.94	0.47	0.60	0.91	0.22	0.68	0.59	0.89	0.88
$-W(C_{\beta}-H_A)^b$	-0.68	-0.04	-0.39	-0.78	-0.02	-0.32	-0.64	0.11	0.84
$-W(C_{\alpha}-N)^c$	1.00	0.84	0.91	0.98	0.88	0.88	0.71	0.95	-0.91
$-\Delta W(C_{\alpha}-N)^c$	1.00	0.72	0.92	0.96	0.84	0.92	0.75	0.78	-0.94
$-W(C_{\beta}-H_{\alpha})^c$	-0.75	-0.04	-0.37	-0.84	-0.07	-0.29	-0.67	0.06	0.84
$-\Delta W(C_{\beta}-H_{\alpha})^c$	-0.30	-0.45	0.58	-0.14	-0.30	0.55	0.21	-0.53	-0.88
$Q(H_A)^c$	0.00	-0.35	0.51	0.17	-0.24	0.47	0.33	-0.44	-0.93
$\Delta Q(H_A)^c$	-0.57	-0.28	0.53	-0.40	-0.19	0.52	0.25	-0.65	-0.98
FED ^c	0.89	0.68	0.38	0.95	0.67	0.29	0.65	0.41	-0.88

^a The signs of quantities are chosen such that the increase in the value corresponds to the increase in the reactivity and *vice versa*; ^b data that relate to the free molecule; ^c data that relate to the model of adsorbed molecule.

its destabilization by adsorption. b) In the structure representing the activated complex in the proposed reaction mechanism (Scheme 1), there proceeds a cyclic transfer of electrons in counter-clockwise manner (Scheme 2). The greater the negative charge on nitrogen atom in isolated amine molecule, the easier these electron transfers in the activated complex.

From Table II and Figs 2 and 3 it becomes evident that experimental data correlate well with calculation, and that independently of the temperature of measurements

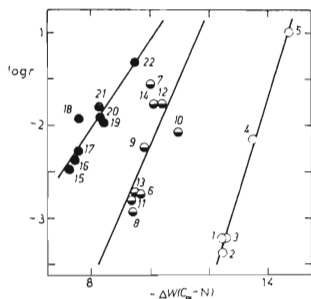


FIG. 2

Calculated relative changes in the strength of the $C_{\alpha}-N$ bond (in per cent) in amine molecule caused by modelling adsorption in correlation with logarithm of the rate of deamination at 555 K. With respect to the symmetry of substitution on nitrogen, the reaction rates for diethylamine and diisopropylamine, resp. triethylamine were corrected by dividing them by a factor of 2 or 3. ○ Primary amines, ● secondary amines, ● tertiary amines; 1 ethyl-, 2 propyl-, 3 butyl-, 4 isopropyl-, 5 tert-butyl-, 6 diethyl-, 7 diisopropyl-, 8 ethylbutyl- (product ethylene), 9 ethylbutyl- (product butene), 10 methylisopropyl-, 11 ethylisopropyl- (ethylene), 12 ethylisopropyl- (propene), 13 isopropylbutyl (butene), 14 isopropylbutyl- (propene), 15 ethylpropylbutyl- (ethylene), 16 ethylpropylbutyl- (propene), 17 ethylpropylbutyl- (butene), 18 triethyl-, 19 dimethylbutyl-, 20 dimethylpropyl-, 21 dimethylethyl-, 22 dimethylisopropylamine

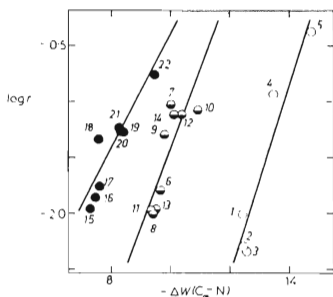
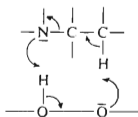


FIG. 3

Calculated relative changes in the strength of the $C_{\alpha}-N$ bond (in per cent) in amine molecule caused by modelling adsorption in correlation with logarithm of the rate of deamination at 590 K. With respect to the symmetry of substitution on nitrogen, the reaction rates for diethylamine, diisopropylamine, resp. triethylamine were corrected by dividing them by a factor of 2 or 3. For designation of points see Fig. 2



SCHEME 2

in the temperature region investigated. Experimental data taken from the work by Catry and Jungers² give less satisfactory correlations, as illustrated in Fig. 4. It is noteworthy that despite of the different behaviour in deamination reaction and likely also despite of the different reaction mechanism, the reactivity of isopropylamine correlates excellently with the reactivities of other primary amines studied (*cf.* Fig. 2).

In conclusion, the use of even very simple models of adsorption makes it possible to describe the behaviour of primary, secondary, and tertiary amines in heterogeneously catalyzed deamination on alumina by the semiempirical CNDO/2 quantum chemical method, and that to a large extent quantitatively. Furthermore, quantum chemical calculations allow to complement, define with more precision and classify the concepts about the reaction course and regularities which control the reaction.

LIST OF SYMBOLS

- B** the basicity of amines (ΔH of the reaction $R^1R^2R^3NH^+ \rightarrow R^1R^2R^3N + H^+$ [kJ/mol])
- FED** frontier electron density in LUMO on H_A [electron charge]

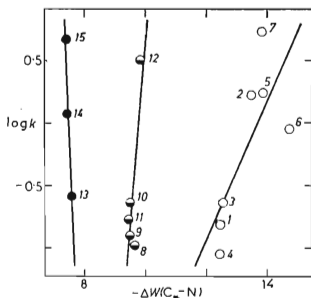


FIG. 4

Calculated relative changes in the strength of the $C_\alpha-N$ bond (in per cent) in amine molecule caused by modelling adsorption in correlation with logarithm of the rate constant of deamination according to Catry and Jungers². With respect to the symmetry of substitution on nitrogen, the rate constants were corrected by dividing them by a factor of 2 and 3, respectively. \circ Primary amines, \bullet secondary amines, \bullet tertiary amines; 1 propyl-, 2 isopropyl-, 3 butyl-, 4 isobutyl-, 5 sec-butyl-, 6 tert-butyl-, 7 cyclohexyl-, 8 diethyl-, 9 dipropyl-, 10 dibutyl-, 11 diisobutyl-, 12 di-sec-butyl-, 13 triethyl-, 14 tripropyl-, 15 tributylamine

k	the rate constant of deamination [cm Hg/min — cf. ref. ²]
$Q(A)$	the charge on atom A [electron charge]
r	the rate of deamination [mol/dm ³ h]
T	absolute temperature [K]
$W(A-B)$	Wiberg index of the bond between atoms A and B

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