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CONVERSIONS IN CATALYTIC DEAMINATION CALCULATED BY STOPPED-FLOW GAS CHROMATOGRAPHY

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SUMMARY

By calculating absolute values for the intercepts of the rate equation that describes the deamination of aminocyclohexane on aluminium oxide, the components of a weighted mean rate constant can be found. From these the conversion of the reactant amine to product(s) can be computed, and this is in good agreement with the conversion determined directly by separate experiments. This is an indication of the internal consistency of the theoretical rate equation, derived on the basis of a particular reaction model with many kinds of active sites. The conversions are much less than 100 %, showing that a considerable fraction of the reactant is adsorbed on sites which transform it to irreversibly adsorbed products. The conversion to gaseous cyclohexene increases with increasing flow-rate of the carrier gas. Finally, it was found that the effective duration of the stops is very different from the real duration.

INTRODUCTION

In a previous paper[1], the detailed kinetics for the deamination of various amines on aluminium oxide and on porous glass, yielding unsaturated hydrocarbons, were reported. The stopped-flow gas chromatographic technique[2,3] was employed, and the results were consistent with the following reaction scheme:

$$A + S^{(i)} \xrightleftharpoons[\text{fast}]{k_A^{(i)}} \underbrace{A\text{–}S^{(i)} \xrightarrow{k_1^{(i)}} B\text{–}S^{(i)} \xrightarrow{k_2^{(i)}} D\text{–}S^{(i)}}_{\text{adsorbed species}} \xrightleftharpoons[\text{fast}]{k_D^{(i)}} D + S^{(i)} \qquad (1)$$

according to which the reacting gaseous amine A is rapidly adsorbed on the *i*th kind of surface active sites with a partition ratio $k_A^{(i)}$, and then gives the adsorbed intermediate B–S$^{(i)}$ with a rate constant $k_1^{(i)}$. The intermediate decomposes, with a rate constant $k_2^{(i)}$, to the adsorbed unsaturated hydrocarbon D–S$^{(i)}$, which is in equilibrium with the gaseous product D, $k_D^{(i)}$ being its partition ratio.

Based on mechanism 1, a theoretical equation was derived, giving the reaction rate, *R*, as a function of the contact time, *t*:

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$$R = \alpha m\left\{\sum_{i=1}^{n} \frac{k_2^{(i)}k_1^{(i)}g^{(i)}}{\bar{k}_1 - k_2^{(i)}} \cdot \exp\left[-k_2^{(i)}t\right] - \left[\sum_{i=1}^{n} \frac{k_2^{(i)}k_1^{(i)}g^{(i)}}{\bar{k}_1 - k_2^{(i)}}\right]\exp(-\bar{k}_1 t)\right\} \qquad (2)$$

where α is a proportionality constant and m the mass of reactant injected, and $g^{(i)}$ and $\bar{k}_1$ are given by the equations

$$g^{(i)} = \frac{k_A^{(i)}}{1 + \sum_{i=1}^{n} k_A^{(i)}} \qquad (3)$$

and

$$\bar{k}_1 = \sum_{i=1}^{n} k_1^{(i)}g^{(i)} \qquad (4)$$

The experimental findings on both surfaces studied[1] require that the first summation in eqn. 2 has only two terms. This can happen in three ways: (a) all $k_2^{(i)}$ with $i \geqslant 3$ tend to infinity or, in physical terms, the rate-determining step on these sites is the formation of the intermediate B–S$^{(i)}$; (b) all $k_1^{(i)}g^{(i)}$ for $i \geqslant 3$ are zero, *i.e.*, the amine adsorbs and reacts only on sites 1 and 2; on all other kinds of sites either it adsorbs reversibly $[g^{(i)} \neq 0]$ but it does not react $[k_1^{(i)} = 0]$, or it does not adsorb at all $[g^{(i)} = 0]$; (c) for $i \geqslant 3$ $k_1^{(i)}g^{(i)} \neq 0$ but $k_2^{(i)} = 0$, *i.e.*, the amine adsorbs and transforms irreversibly to B–S$^{(i)}$, but this does not yield gaseous products.

In all studies published so far in which the stopped-flow technique was employed, the various rate constants k were accurately determined from the slopes of plots of ln R against t; however, for the pre-exponential factors of eqn. 2:

$$a^{(i)} = \frac{k_2^{(i)}k_1^{(i)}g^{(i)}}{\bar{k}_1 - k_2^{(i)}} \qquad (5)$$

only *relative* values were determined. These relative values permit us to decide whether possibility (a) above is substantiated or not, but they do not allow us to distinguish between possibilities (b) and (c), because in both instances the pre-exponential factor of the negative term in eqn. 2 is equal to the sum of the values of the other two pre-exponential factors, and this was found to hold for deaminations on aluminium oxide[1]. In contrast, in case (a) the second summation of eqn. 2 contains terms $-k_1^{(i)}g^{(i)}$ with $i \geqslant 3$, which make the summation smaller (absolutely) than the sum of the $a^{(i)}$s of the other two terms. This happens in deaminations on porous glass[1].

The distinction between possibilities (b) and (c) is important, as it affects not the rate constants of the reactions but the extent of *conversion* of amine into the desired product. This can be seen by integrating with respect to t the expression in braces { } on the right-hand side of eqn. 2, between the limits 0 and ∞, obtaining unity in case (b), *i.e.*, 100% conversion, whereas in case (c) the result is

$$\text{conversion} = \frac{k_1^{(1)}g^{(1)} + k_1^{(2)}g^{(2)}}{\sum_{i=1}^{n} k_1^{(i)}g^{(i)}} < 1 \qquad (6)$$

i.e., less than 100%. Experimentally, this can be done either by calculating the conversion directly from the chromatogram, or by finding the *absolute* values of the pre-exponential factors $a^{(i)}$, calculating from them $k_1^{(i)}g^{(i)}$ by eqn. 5, and then computing the conversion by means of eqn. 6. The denominator of eqn. 6 is $\bar{k}_1$, according to eqn. 4. The latter method, *i.e.*, through the absolute $a^{(i)}$ values, will demonstrate the internal consistency of the theory underlying eqn. 2, and also its potential for calculating not only rate constants but also conversions through the rate constants.

It is the object of this paper to demonstrate these further potentialities of the stopped-flow technique, by applying the above considerations to a specific case, namely the deamination of aminocyclohexane on aluminium oxide, where the experimental data bear out possibilities (b) or (c) mentioned above.

EXPERIMENTAL

Active aluminium oxide of Brockmann activity II was obtained from BDH (Poole, Great Britain) and sieved to 100–150 mesh. Aminocyclohexane and cyclohexene were purchased from Fluka (Buchs, Switzerland) and were of Purum grade. Nitrogen (99.999% purity) from Linde (Athens, Greece) was used as the carrier gas, after drying it by passage through a tube of 4A molecular sieve.

The apparatus has been described elsewhere[1]. The catalytic column (glass, 1 m × 4.2 mm I.D., filled with aluminium oxide) was conditioned by heating it *in situ* at 543 or 673°K for 24 h under a flow of carrier gas.

Numerical integrations and other calculations were performed on a Hewlett-Packard 9825A desk-top computer connected with a 9872B plotter.

RESULTS AND DISCUSSION

All runs were conducted at 543.2°K. The main product was cyclohexene with a trace amount of benzene. All rate constants reported here refer to the formation of cyclohexene. If h denotes the height of the stop-peaks in centimetres which is proportional to the reaction rate R, the ln (h/cm) *versus* time curves, after a small initial rise, fall off as a sum of two exponential functions. From this behaviour, two rate constants are extracted, as described in detail elsewhere[1]. This corresponds to the first summation in eqn. 2, and the last negative term is responsible for the initial rise.

The effect of the activation temperature of aluminium oxide on the rate constants, as well as the effect of the number of amine injections, were examined first. The catalyst was heated *in situ* for 24 h under a flow of carrier gas, first at 543°K, then at 673°K, and then again at 673°K. Between two successive activations several kinetic experiments were conducted, always at 543.2°K. A t-test of significance was performed on the mean values of the rate constants $k_2^{(1)}$ and $k_2^{(2)}$, calculated from six, seven or nine kinetic runs, for each activation temperature, and this showed that the differences in the $k_2^{(1)}$ values (calculated from the tail of the curves) are not statistically significant at the 10% probability level, whereas the differences in the $k_2^{(2)}$ values are not significant at the 5% or 2% level. This indicates that the effect of the activation temperature on the rate constants is small. The number of injections of the reactant amine on to the catalyst also has a small effect, as judged by the unbiased estimate of the standard deviation of the rate constants for each activation temperature. This was found to be 8.1–23.4% of the respective mean value. Thus, self-poisoning effects of the catalyst by the reacting amine or the ammonia produced by the reaction are negligible. This conclusion was further confirmed by injecting gaseous ammonia (1 and 5 cm^3 at atmospheric pressure) on to the catalytic column and after 24 h conducting kinetic runs with aminocyclohexane. No significant change in the rate constants was observed.

After these preliminary experiments, the absolute values of the pre-exponential factors $a^{(i)}$ given by eqn. 5 were determined using the equation

$$a^{(i)}_{\text{abs}}/\text{sec}^{-1} = [a^{(i)}_{\text{rel}}/\text{cm}] \cdot \frac{(w_{\frac{1}{2}}/\text{sec})\ 1.064}{(m/\text{mol})\ (t_s/\text{sec})\ (S/\text{cm sec mol}^{-1})} \tag{7}$$

$a^{(i)}_{\text{rel}}$ are the relative values of the pre-exponential factors in eqn. 2, as determined from the intercepts of ln (h/cm) against time plots, $w_{\frac{1}{2}}$ is the half-width of the stop-peaks, 1.064 is a factor for finding the area under the stop-peaks from their height and their half-width, m the mass of the reactant injected, t_s the duration of each stop and S the response of the flame-ionization detector.

The effective value of t_s does not necessarily coincide with the real time during which the valves supplying the carrier gas are closed, as measured by a watch, and it can be calculated as follows. After injecting 0.5 mm^3 of amine and performing several stops of the carrier gas until the chromatographic signal decays to a negligible height, the total amount of products is given by the integral

$$A = \int_0^\infty R\,\mathrm{d}t = \int_0^\infty \frac{1.064\ hw_{\frac{1}{2}}}{t_s} \cdot \mathrm{d}t = \frac{1.064\ w_{\frac{1}{2}}}{t_s} \int_0^\infty h\,\mathrm{d}t \tag{8}$$

where R is the rate of the reaction, t the time of carrier gas stop and the other symbols have the meanings explained previously. The value of A is found from the total area under the elution curve, which can be measured by a disc integrator. The integral on the far right of eqn. 8 can be found by numerical integration with respect to time of the stop-peak height h above the continuous elution curve. As $w_{\frac{1}{2}}$ is known from the chromatogram, t_s can be calculated, taking care to change A/counts to A/cm sec, *i.e.* to the same units as $\int_0^\infty h\mathrm{d}t$.

Finally, the response S in eqn. 7 was found by injecting known amounts of the pure product into an empty column and integrating the resulting elution curve. This was done for various flow-rate ratios of hydrogen and carrier gas. As expected, the maximum response was found for equal flow-rates of the two gases.

After the above, $a^{(i)}_{\text{abs}}$ was found for two carrier gas flow-rates. The results, together with the various physical quantities used in the calculations and the respective rate constants, are given in Table I. An accurate value for the weighted mean rate constant $\bar{k}_1$ could not be determined from the ascending initial part of the experimental curves. The value given in Table I was found using the same experimental conditions but a different method, the so-called reversed-flow gas chromatography[4]. The other two rate constants, $k_2^{(1)}$ and $k_2^{(2)}$, determined by the latter method have about the same values as those found by the stopped-flow technique.

The next two steps were to calculate $k_1^{(i)}\,g^{(i)}$ from $a^{(i)}_{\text{abs}}$ using eqn. 5, and then the conversion by means of eqn. 6. Their values are also given in Table I.

TABLE I

PHYSICAL QUANTITIES CALCULATED FOR THE DEAMINATION OF AMINOCYCLOHEXANE ($4.13 \cdot 10^{-6}$ mol) TO CYCLOHEXENE, AT 543.2°K, ON ALUMINIUM OXIDE ACTIVATED AT 673°K FOR 24 h

Two corrected volume flow-rates of the carrier gas were used, and the stop durations (real) were 60 sec.

Parameter	*Flow-rate, $\dot{V}$ (cm³ sec⁻¹)*	
	0.191	*0.975*
$10^4\,k_2^{(1)}$ (sec^{-1}), rate constant	1.69 ± 0.05	1.55 ± 0.01
$10^4\,k_2^{(2)}$ (sec^{-1}), rate constant	5.8 ± 0.1	5.8 ± 0.3
$10^3\bar{k}_1$ (sec^{-1}), weighed mean rate constant*	2.65	
t_s (sec), effective stop duration	15.4	21.8
$w_{\frac{1}{2}}$ (sec), stop-peak half-width	36	9
S (cm sec mol^{-1}), detector response	$5.36 \cdot 10^{13}$	$3.53 \cdot 10^{13}$
$a_{\mathrm{rel}}^{(1)}$ (cm), relative intercept	924.7	9657.7
$a_{\mathrm{rel}}^{(2)}$ (cm), relative intercept	6612.2	33323.2
$10^5\,a_{\mathrm{abs}}^{(1)}$ (sec^{-1}), absolute intercept	1.039	2.910
$10^5\,a_{\mathrm{abs}}^{(2)}$ (sec^{-1}), absolute intercept	7.429	10.04
$10^4\,k_1^{(1)}\,g^{(1)}$ (sec^{-1}), calculated from eqn. 5	1.53	4.68
$10^4\,k_1^{(2)}\,g^{(2)}$ (sec^{-1}), calculated from eqn. 5	2.65	3.58
Conversion (%) calculated from eqn. 6	15.8	31.2
Conversion (%) found experimentally	18.9	32.3

* This was found from a separate experiment using the reversed-flow technique (see text).

Finally, the conversion for both flow-rates was determined in separate experiments directly by performing deaminations without stops, finding the area under the product elution curve with a disc integrator and comparing it with the elution curve area of a known amount of pure cyclohexene injected directly on to the same catalytic column. Experiments with pure cyclohexene injected into an empty column showed that the amount of cyclohexene adsorbed irreversibly on the aluminium oxide surface was only 3–5%.

From the results in Table I the following conclusions can be drawn. The reaction model described by eqn. 1 leads to a theoretical rate equation (eqn. 2) which is internally consistent in that it not only explains the time dependence of the rate for the deamination reactions permitting the calculation of rate constants, but it also, through its pre-exponential factors, correlates these rate constants with the total conversion of the reactant to products. This is accomplished by finding the absolute values of the intercepts of eqn. 2 by means of eqn. 7. The calculated conversions are in good agreement with those found experimentally.

From the conversions found or calculated, details of the mechanism emerge, *viz.*, that deamination takes place on two kinds of active sites of aluminium oxide, but a considerable fraction of the reacting amine adsorbs on other kinds of sites and transforms irreversibly to other adsorbed products [case (c) mentioned in the Introduction].

With the help of $a_{\mathrm{abs}}^{(i)}$, using eqn. 5, two components $k_1^{(i)}\,g^{(i)}$ can be extracted from the weighted mean rate constant $\bar{k}_1$, and these increase with increasing flow-rate, leading to increased conversions. As pure rate constants, such as $k_2^{(i)}$, do not seem to change appreciably with the flow-rate, an explanation of why $k_1^{(i)} g^{(i)}$ changes is that $g^{(i)}$ increases with increasing flow-rate. This can be due to changes in the apparent values of the partition ratios, $k_A^{(i)}$, because of changes in the column performance with rate.

A final comment concerning the stopped-flow technique is that the effective duration of stops, t_s, is very different from the real duration.

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