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On the Mechanism of Reversible Unimolecular Reactions and the Canonical ("High Pressure") Limit of the Rate Coefficient at Low Pressures*)

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Chemical Kinetics / Elementary Reactions

Jost's [1] treatment of generalized first order kinetics is used for a new discussion of the mechanism of reversible unimolecualar reactions. A detailed analysis of time dependent average microscopic rate coefficients and level populations is presented using exact solutions for a realistic model of an isomerization reaction. It is shown that unimolecular fall-off for the macroscopic relaxation is not mainly due to a reduced population of reactive levels as suggested by the irreversible Lindemann mechanism, but rather due to a fast reverse reaction even at early times. It is furthermore shown that the average microscopic rate coefficients can be measured directly, in principle. At equilibrium they are equal to the canonical ("high pressure") limit of the rate coefficient even for arbitrarily low pressures. Practical experimental schemes are suggested for thus obtaining high pressure limiting rate coefficients without extrapolation procedures.

1. Introduction

In 1947 Jost [1 – 3] presented a treatment of generalized first order kinetics. One possible application of this treatment is a new discussion of the mechanism of gas phase unimolecular reactions. The current understanding of these reactions is based on the Lindemann [4] mechanism:

$$A_J + M \underset{\kappa_{JI}}{\overset{\kappa_{IJ}}{\rightleftarrows}} A_I^* + M \tag{1a}$$

$$A_I^* \quad \xrightarrow[k_I^*]{} B_L \tag{1b}$$

$$k_{\mathrm{uni}}([M]) = \lim_{t \to \infty} \frac{\mathrm{d}}{\mathrm{d}t}\{-\ln(\sum [A_J] + \sum [A_I^*])\}\,. \tag{1c}$$

This mechanism was proposed by Lindemann in view of two main consequences: 1. It correctly *explained* the independence of the effective unimolecular rate coefficient upon the concentration [M] of the collision partner at high pressures (previous explanations for this were based upon the "radiation theory of chemical action" [5, 6]). 2. It *predicted* the fall-off of the effective unimolecular rate coefficient at low [M]. This was later established experimentally. In this framework the mechanistic explanation of the fall-off is straightforward [7]: At high pressures the reactive levels A_I^* are in Boltzmann equilibrium with the levels A_J, because (1a) establishes a fast prequilibrium, and with many levels N one has the Boltzmann average:

$$\lim_{[M] \to \infty} (k_{\mathrm{uni}}) \equiv k_\infty \equiv k^{\mathrm{eq}} = \sum_N q_N^{\mathrm{eq}} k_N^* \tag{2}$$

(k_∞ stands for infinite or high pressure limit, which is also the canonical equilibrium limit k^{eq}).

At low [M] the reaction (1a) becomes rate determining and the reactive states are depleted more rapidly than they become repopulated by collisions with M. The unimolecular steady-state rate coefficient is smaller than its equilibrium or high pressure value, because the steady state population $q_N^{\mathrm{st}} < q_N^{\mathrm{eq}}$ for reactive levels N:

$$k_{\mathrm{uni}}([M]) = \sum_N q_N^{\mathrm{st}} k_N^* < k_\infty = k^{\mathrm{eq}}\,. \tag{3}$$

This view of the unimolecular fall-off has been maintained for six decades after Lindemann. An important addition has been the RRKM theory [8], that is the application of transition state theory for the calculation of the k_N^* combined with the strong collision assumption. Furthermore, the extension to multilevel systems has also introduced nonequilibrium effects for *non-reactive* levels (weak collision effects [9]). An excellent recent discussion of this view of the fall-off can be found in Ref. [9] and there exist several more recent reviews and books [10 – 13].

In the present investigation we have revisited the mechanism of unimolecular reactions for a number of reasons: 1. The extrapolation to high pressures (i.e. to $k_\infty = k^{\mathrm{eq}}$) is a fundamental challenge and presents notorious practial problems, particularly at high temperatures for large molecules [10 – 14], but also for certain fast reactions occurring at room temperature [15]. 2. Eq. (1) describes only the forward part of the mechanism. It seems desirable to have a consistent detailed treatment of reversible unimolecular reactions for the application of small perturbation, fast relaxation methods [16, 17]. 3. The consideration of a reversible mechanism, which has universal validity, may also shed new light on the detailed mechanism of unimolecular processes in general.

We shall therefore consider here the general reversible mechanism (in symbolic notation allowing for many levels):

$$A_J + M \underset{\kappa_{JI}}{\overset{\kappa_{IJ}}{\rightleftarrows}} A_I^* + M \tag{4a}$$

$$A_I^* \quad \underset{\kappa_{IL}^*}{\overset{\kappa_{LI}^*}{\rightleftarrows}} B_L^* \tag{4b}$$

$$B_L^* + M \underset{\kappa_{LN}}{\overset{\kappa_{NL}}{\rightleftarrows}} B_N + M\,. \tag{4c}$$

A thorough discussion of measurable average rate coefficients in such a mechanism will lead us to the following striking con-

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*) Teil 8 des Vortrages „Einfache kinetische Modelle molekularer Prozesse", gehalten in Göttingen am 16. Juni 1983 aus Anlaß des 80. Geburtstages von Wilhelm Jost.

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clusions: 1. It is possible to derive schemes by which the "high pressure" or canonical rate coefficient can be measured at low pressures. That is, unimolecular fall-off can be circumvented. 2. The view that unimolecualar fall-off is due to the reduced population of reactive levels is incomplete, since this effect often is only the minor of two contributions to the fall-off.

The present paper is a first of a series. In the following publications [15] reversible unimolecular reactions induced by monochromatic infrared radiation and collisionfree intramolecular dynamics will be considered along the same lines, including the consequences of non-Pauli behaviour. It will furthermore be shown when and why the "irreversible" mechanism, Eq. (1), commonly used in theoretical calculations, is suitable for obtaining experimental relaxation rate coefficients.

2. The Definition of the Rate Coefficients and Their Time Dependence

In order to put life into the abstract considerations, Fig. 1 illustrates the general Eq. (4) for a model isomerization, for which explicit results will be given below. The molecular parameters are of no particular concern, but the reader may have in mind a cis-trans isomerization similar to the one in 1,2-dichloroethylene, which has been investigated experimentally in thermal systems [18] and which is of interest also in unimolecular reactions induced by monochromatic infrared radiation [19, 20]. Fig. 1 shows various excitation levels for isomers A and B. The kinetics is supposed to be described by generalized first order kinetics [1], which we write in matrix notation for brevity:

$$\dot{\boldsymbol{p}} = \boldsymbol{K}\boldsymbol{p} \tag{5}$$

$$\boldsymbol{p}(t) = \exp(\boldsymbol{K}t)\,\boldsymbol{p}(0)\,. \tag{6}$$

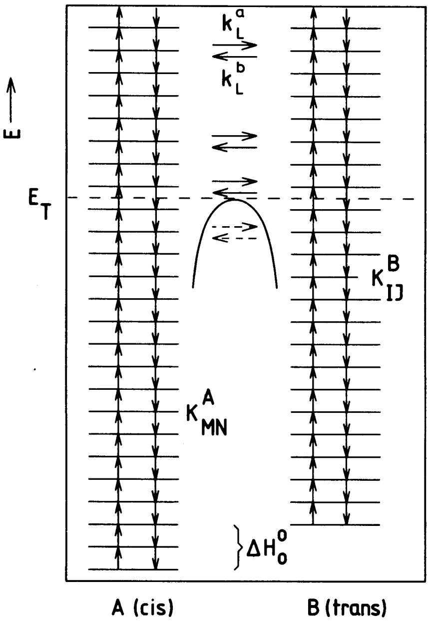

Fig. 1
Scheme for a model reversible isomerization reaction described by a master equation (see also explanations in the text)

We shall present below the exact analytical solution, Eq. (6), for realistic model systems, although simple closed expressions can be derived for some simplified models which would contain part of the essence of the effects to be observed. The p_L are level populations in the total, combined system and we use the notation p_L^X with X = A or B to denote restriction to one isomer with appropriate redefinition of the indices. We shall make use also of relative level populations q for either isomer

$$q_L^X = p_L^X / \sum_J{}' p_J^X \tag{7a}$$

and of concentration variables c (in cm^{-3}, for example):

$$p_L = c_L / \sum_L c_L \tag{7b}$$

$$c_X = \sum_{L(X)}{}' c_L^X \tag{7c}$$

$$c = c_A + c_B\,.$$

The Σ' denotes summation for levels of one isomer only. The rate coefficients for collisional transitions are computed separately for the A and B ladders:

$$K_{LN}^X = \left(\frac{8kT}{\pi\mu}\right)^{1/2} \int_0^\infty \sigma_{LN}^X \left(\frac{E}{kT}\right) \exp\left(-\frac{E}{kT}\right) \left(\frac{dE}{kT}\right) [M]\,. \tag{8}$$

[M] is the concentration of a solvent gas in large excess. σ_{LN}^X is the energy dependent integral cross section for energy transfer in collisions with M, averaged over initial states in the level N and summed over final states in level L. The K_{LN}^X satisfy the detailed balance relationship, Eq. (9):

$$\frac{K_{LN}^X}{K_{NL}^X} = \frac{\rho_L^X}{\rho_N^X} \exp[-(E_L - E_N)/kT] \tag{9}$$

with the density of states ρ_L^X in level L (or the state number in a discrete picture). The specific rate coefficients $k_L^X \equiv K_{IJ}^*$ for collisionless reaction above the threshold energy E_T (and slow tunneling below E_T) are supposed to be calculated from an intramolecular Pauli equation [15, 21] or from ordinary statistical rate theory (RRKM [8] or statistical adiabatic channel model [11]). They then satisfy the detailed balance relationship (level index L referring to the same E):

$$k_L^a / k_L^b = \rho_L^B / \rho_L^A\,. \tag{10}$$

Although this has been used in our model below, most of the conclusions remain valid if the right hand side of Eq. (10) is multiplied by a factor g_L, as is necessary, for instance, when an intramolecular case C master equation applies [15, 22]. The only essential assumption is the applicability of generalized first order kinetics, Eqs. (5) and (6). This is expected to hold for the collisional process with a large excess of M and presumably also for the description of the intramolecular process [21]. The diagonal elements of $\boldsymbol{K}$ in Eq. (5) are, from conservation of probability:

$$K_{RR} = -\sum_S K_{SR}\,. \tag{11}$$

Here we have general matrix elements including transitions between the isomers and an unrestricted sum. This completes the definition of the model.

In a macroscopic relaxation experiment the measurable quantities are the relaxation times $t_j > 0$, which are given through the corresponding eigenvalues λ_j of $\boldsymbol{K}$ [17, 24]:

$$t_j = -1/\lambda_j \,. \tag{12}$$

One has $\lambda_0 = 0$ for the largest eigenvalue with the corresponding equilibrium eigenvector. The first relaxation eigenvalue $\lambda_1 < 0$ is minus the relaxation rate coefficient k_r and usually set equal to the apparent steady state reaction rate coefficient for irreversible reactions with an equilibrium constant $K_C \gg 1$ (we shall come back to this point below). Its reduced pressure dependence is shown by the lower, curved function in Fig. 2 in a typical reduced, double logarithmic fall-off plot [10]. The points are from the exact solution of the master equation for the model, for the computational techniques see Ref. [22]. As expected $-\lambda_1$ is proportional to pressure at low P (low pressure limit) and independent of pressure at high P (high pressure limit), with a transition in between. In that sense the results in Fig. 2 are completely traditional. However, Fig. 2 shows a modification of this view at low P, when radiative transition $K_{\mathrm{LM}}^{\mathrm{X,rad}}$ are included [23]. Then at low P (points marked "rad") $-\lambda_1$ becomes independent of pressure, in agreement with Perrin's view. This regime should be just about accessible with current experimental techniques [23]. We shall not consider this modification of the Lindemann mechanism in detail here, but rather a more surprising one.

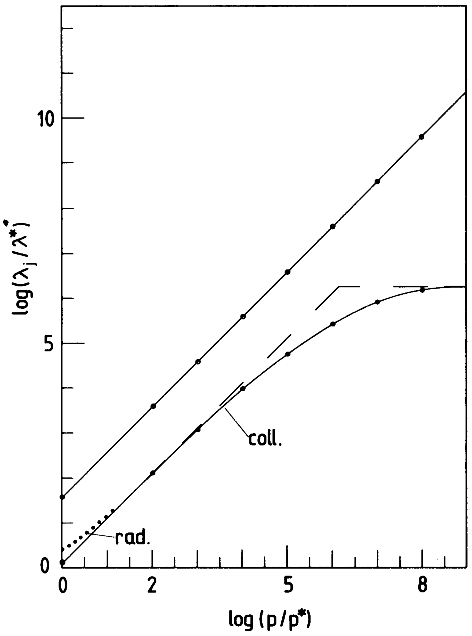

Fig. 2
First ($-\lambda_1$, lower function) and second ($-\lambda_2$, upper function) relaxation eigenvalues for the model in Fig. 1 as a function of solvent gas pressure p. The points are computed from exact solutions of the master equation, the lines are drawn for easy visibility only. $-\lambda_1$ shows the characteristic fall-off whereas $-\lambda_2$ is proportional to p in the whole range shown

The relaxation eigenvalues λ give information about the measurable relaxation of macroscopic parameters in a reactive system which is not in equilibrium. We focus now attention upon the microscopic rate processes, which occur for systems which may or may not be in equilibrium. For a careful definition of an average, microscopic rate coefficient we consider an observer at the top of the barrier in Fig. 1, who counts the molecules crossing the barrier from A to B and the reverse. We can imagine at this point the observer to be a fast student with particular abilities. Realistic experimental methods will be discussed below. In order to avoid ambiguities, we shall assume that the mean residence time at A or B is long compared to the crossing time over the barrier. It can be shown that for our purposes the uncertainty principle does not restrict the observation in an essential way.

Considering the time derivatives of total concentrations c_{A} or probabilities $p_{\mathrm{A}} = c_{\mathrm{A}}/(c_{\mathrm{A}} + c_{\mathrm{B}})$ the *net* reaction rate or the *net* number of forward reactive events per unit volume can be written with the usual kinetic conventions using the difference of forward and backward rate processes:

$$-\frac{\mathrm{d}c_{\mathrm{A}}}{\mathrm{d}t} = k_{\mathrm{a}}\, c_{\mathrm{A}} - k_{\mathrm{b}}\, c_{\mathrm{B}} \tag{13}$$

with

$$k_{\mathrm{a}} = \sum_{\mathrm{J}}{}' \, q_{\mathrm{J}}^{\mathrm{A}}\, k_{\mathrm{J}}^{\mathrm{a}} \tag{14a}$$

$$k_{\mathrm{b}} = \sum_{\mathrm{L}}{}' \, q_{\mathrm{L}}^{\mathrm{B}}\, k_{\mathrm{L}}^{\mathrm{b}} \,. \tag{14b}$$

The rate coefficient of reactive events in either forward or backward direction is

$$k_{\mathrm{s}} = k_{\mathrm{a}} + k_{\mathrm{b}} \,. \tag{15}$$

This is by our definition the number of reactive events per unit time and per molecule. Because the relative populations $q_{\mathrm{J}}^{\mathrm{X}}$ are time dependent, the rate coefficients k_{a}, k_{b}, and k_{s} are also time dependent. At equilibrium (as $t \to \infty$) one has

$$k_{\mathrm{a}}^{\mathrm{eq}} = \sum{}' \, q_{\mathrm{J}}^{\mathrm{Aeq}}\, k_{\mathrm{J}}^{\mathrm{a}} \tag{16a}$$

$$q_{\mathrm{J}}^{\mathrm{Aeq}} = \rho_{\mathrm{J}}^{\mathrm{A}} \exp(-E_{\mathrm{J}}^{\mathrm{A}}/kT) / \sum_{\mathrm{J}}{}' \, \rho_{\mathrm{J}}^{\mathrm{A}} \exp(-E_{\mathrm{J}}^{\mathrm{A}}/kT) \tag{16b}$$

$$k_{\mathrm{a}}^{\mathrm{eq}}/k_{\mathrm{b}}^{\mathrm{eq}} \equiv K_{\mathrm{c}} = \sum_{\mathrm{J}}{}' \, p_{\mathrm{J}}^{\mathrm{Aeq}} / \sum_{\mathrm{L}}{}' \, p_{\mathrm{L}}^{\mathrm{Beq}} \,. \tag{16c}$$

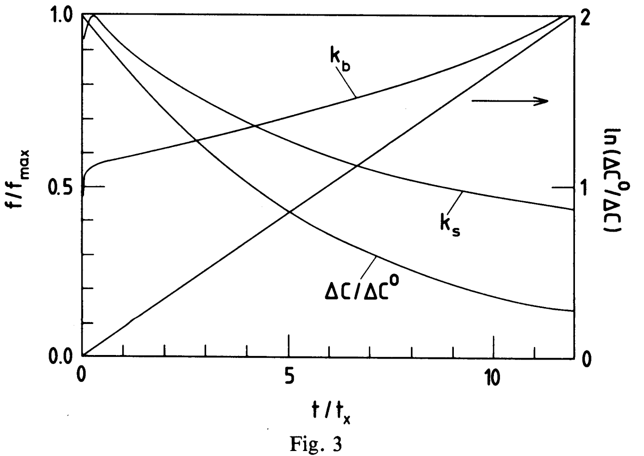

Fig. 3
Relaxation of $\Delta c/\Delta c^0$, $\ln(\Delta c^0/\Delta c)$, $k_{\mathrm{b}}(t)$ and $k_{\mathrm{s}}(t)$ for the model reaction, starting with trans at 1200 K and low pressures. The functions corresponding to the left hand ordinate are normalized to their maximum values ($= 1$ for $\Delta c/\Delta c^0$, $= 3.08 \cdot 10^4\ \mathrm{s}^{-1}$ for k_{b} and $= 3.4 \cdot 10^4\ \mathrm{s}^{-1}$ for k_{s}) see also the explanations in the text

Eqs. (16a – c) imply, that the rate coefficients defined by the rate of reactive events at equilibrium are equal to the canonical equilibrium value (i.e. the high pressure limit). When one measures these in the ideal gas phase there is no pressure dependence and in particular no Lindemann fall-off.

Fig. 3 shows results for the model system, which illustrate these rate coefficients for a large initial displacement from equilibrium (the reaction considered is pure trans → cis after shock heating to 1200 K at low pressures) $\Delta c/\Delta c^0$ and $\ln(\Delta c^0/\Delta c)$ show practically exponential relaxation towards equilibrium, i.e. the reaction occurs near steady state, dominated by a single relaxation eigenvalue $-\lambda_1$ and with negligible τ_1 according to Eq. (17):

$$\Delta c = c(t) - c^{\mathrm{eq}} = \Delta c^0 \exp[\lambda_1 (t - \tau_1)] . \tag{17}$$

Nevertheless, the rate coefficients k_S and k_b are strongly time dependent, relaxing towards their equilibrium value as $\Delta c/\Delta c^0$ approaches zero. All functions in Fig. 3 have been normalized to their maximum values, in particular $k_b^{\max} = 3.1 \cdot 10^4\ \mathrm{s}^{-1}$ and $k_s^{\max} = 3.4 \cdot 10^4\ \mathrm{s}^{-1}$. This can be compared to the relaxation coefficient $k_r = 0.17\ \mathrm{s}^{-1}$:

$$k_r(\mathrm{st}) = -\lambda_1 = \lim_{t\to\infty} \left\{ -\frac{\mathrm{d}}{\mathrm{d}t} \ln(\Delta c/\Delta c^0) \right\} \tag{18}$$

k_r is more than five orders of magnitude smaller than the total reaction rate coefficient k_S for this realistic model system. The relaxation rate arises from the small difference of two large reaction rates. (We use k_r or $k_r(\mathrm{st})$ for the steady state value and $k_r(t)$ for the time dependent value of the rate coefficient defined by the argument in Eq. (18)). Fig. 4 gives further illustration of the relaxation towards the equilibrium values for the same conditions by showing the logarithm of the ratios of the relevant quantities and their respective equilibrium values. It is seen that there is still appreciable time dependence at times when the initial displacement from equilibrium has decayed to $1/e$ and to $1/e^2$. At all practically important times the reaction rate coefficients are much larger than k_r.

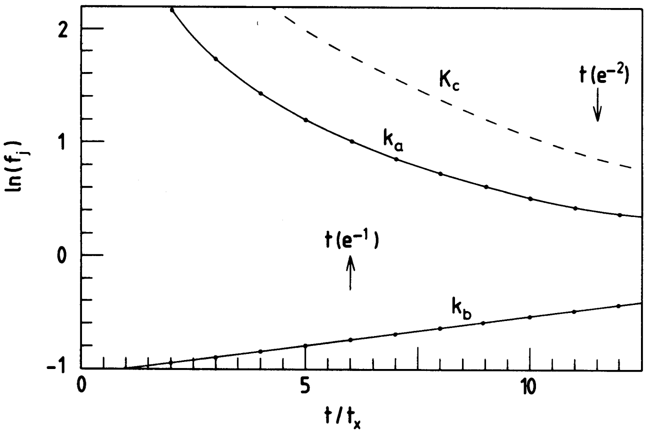

Fig. 4
Parameters of the model reactions with the conditions of Fig. 3; $\ln(k_a(t)/k_a^{\mathrm{eq}})$, labelled k_a, $\ln(k_b(t)/k_b^{\mathrm{eq}})$, labelled k_b and $\ln[K_C^{-1}\, k_a(t)/k_b(t)]$, labelled K_C

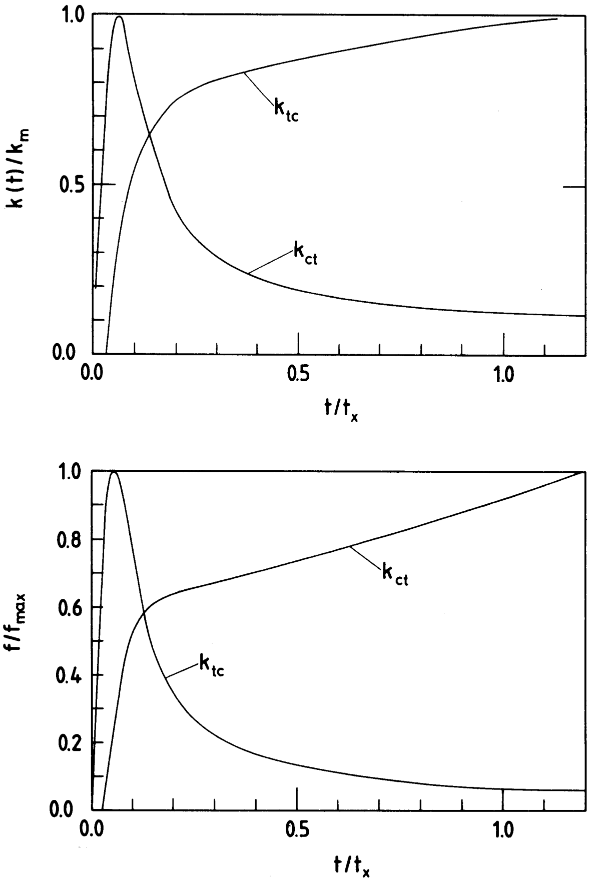

Fig. 5
Time dependent rate coefficients k_{tc} and k_{ct} for the model reaction at 1500 K and low pressures.
a) starting with pure trans; b) starting with pure cis
The rate coefficients are all normalized to their individual maximum values within the range shown

Figs. 3 and 4 correspond essentially to steady state behaviour. Fig. 5 shows a more detailed view of the initial transient period, which is more important at high temperatures (here for the model reaction at 1500 K and low pressures). Average rate coefficients $k_a \equiv k_{tc}$ and $k_b \equiv k_{ct}$, Eq. (14), are shown for either starting with the cis or trans isomer. This gives an interesting insight into the mechanism of the reaction.

In the early stages the back reaction (as defined from the initially present isomer) has a pronounced maximum in the rate coefficient. This balances the fact that the concentration of the corresponding isomer is small initially. Therefore the rates $k_a c_A$ and $k_b c_B$ in Eq. (13) are of similar magnitude after a short time. The view that, starting with A, for instance, the term $k_b c_B$ in Eq. (13) could be neglected in the early stages of the reaction is completely misleading, if true reaction rates are considered (see also below).

Fig. 6 shows the time dependence of the relaxation rate coefficient k_r under the conditions of a typical T-jump relaxation experiment with small initial displacement from equilibrium [16, 17] (Here, for the model, an equilibrium mixture at 1400 K has been suddenly heated to 1500 K). It is seen that k_r relaxes rather quickly to its steady state value. It is this quick relaxation that should be compared to the initial transients or incubation phenomena discussed in the framework of the irreversible mechanism of unimolecular reactions [11, 25 – 28]. Under most ordinary conditions it is of little importance in thermal systems at moderate temperature. An exception is the mechanism of unimolecular reactions induced by monochromatic infrared radiation, where the initial transients are an essential phenomenon [20 – 23].

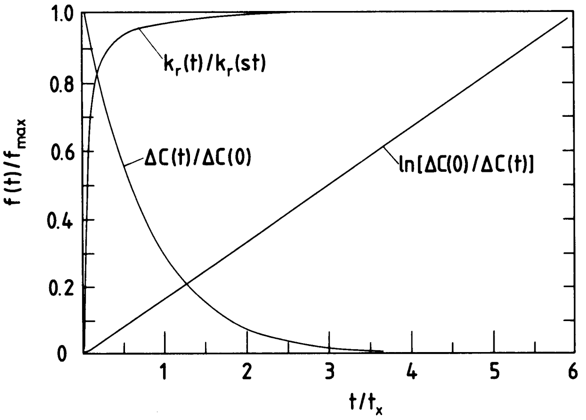

Fig. 6
Relaxation experiment for the model reaction (T jump from a 1400 K equilibrium mixture to 1500 K). The functions indicated in the figure have all been normalized to their individual maximum values (see also discussion in the text)

At this point it is necessary to establish the relationship to the standard evaluation of relaxation experiments in terms of apparent rate constants which are *not* equal to the rate coefficients k_a and k_b. From the measured k_r(st) and K_C one chooses to define [16, 17]:

$$\bar{k}_a \equiv k_r/(1 + 1/K_C) \tag{19a}$$

$$\bar{k}_b \equiv k_r/(1 + K_C)\,. \tag{19b}$$

The $\bar{k}_a$ and $\bar{k}_b$ are defined in such a way that they satisfy an apparent rate law like Eq. (13) with time independent $\bar{k}_a$ and $\bar{k}_b$ and the "detailed balance", Eq. (16c). At the high pressure limit one has $k_a = \bar{k}_a = k_a^{eq}$ and $k_b = \bar{k}_b = k_b^{eq}$. The Eqs. (19) have usually been used for condensed phase relaxation experiments, where these equalities may or may not be true. However, certainly in low pressure gas phase experiments $\bar{k}_a$ and $\bar{k}_b$ have no direct relationship to the true rate of reaction events and are best conceived to be a replacement of the measurable pair of quantities (k_r, K_C) by a new pair of quantities ($\bar{k}_a$, $\bar{k}_b$). This fact has probably been generally appreciated, certainly after the work of Puyn and Ross [29], which is related to earlier suggestions implicit in the papers of Jost [1], Zwolinsky, and Eyring [3], Eigen [17], Polanyi [30], Ross, and Mazur [31], Rice [32], and Widom [33]. Subsequent work has concentrated on the deviation of the apparent $\bar{k}_a$ and $\bar{k}_b$ from the more fundamental k_a^{eq} and k_b^{eq} (see also the recent discussion for nonlinear systems by Lim and Truhlar [34]). This is also in the line of the usual consideration of the irreversible mechanism of unimolecular reactions [10 – 12], for which by definition $k_r = \bar{k}_a$. An interesting question is, of course, why and when the common theoretical calculation of k_r, using the irreversible model [13, 35] for both parts of a reversible reaction, gives correct results. This question is best discussed separately [15]. Here we wish to stress the important role played by the *true* k_a and k_b and their time dependence for understanding the mechanism of unimolecular reactions. Further insight is gained from the consideration of level populations in the course of the reaction.

3. Analysis of the Time Dependent and Steady State Populations

The time dependence of the average rate coefficients k_a and k_b arises from the time dependence of the relative level populations, because the specific level rate coefficients k_L^a and k_J^b are supposed to be constant (more generally k_L^a and k_J^b are time dependent as well [21], but not importantly so for the present considerations). Therefore, a microscopic look at the reaction would be incomplete without the consideration of the individual level populations. The analytical steady state result from the master Eq. (6) is given by Eq. (20) [1, 16, 17, 24]:

$$p_J(t) - p_J^{eq} = (p_J^0 - p_J^{eq}) \exp[\lambda_1 (t - \tau_1)]\,. \tag{20}$$

Fig. 7 shows the populations calculated exactly for the transient period in our model for the trans → cis conversion at 1500 K and low pressures (starting from pure trans, at a time with $k_r(t) \simeq k_r(\mathrm{st})/2$). In Fig. 7a the transient populations of trans levels are compared to their equilibrium value. There is a

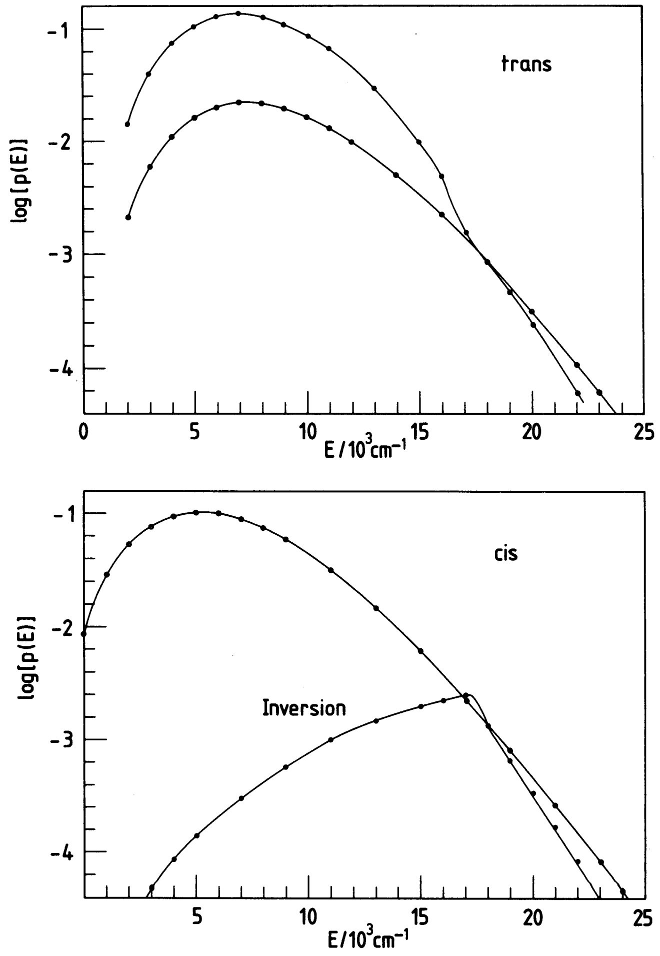

Fig. 7
Level populations p for the transient period of the model reaction at 1500 K (starting with pure trans).

a) Populations of trans levels compared to the thermal populations at 1500 K.

b) Populations of cis levels compared to the thermal populations at 1500 K large overpopulation of low energy trans levels, whereas the population of reactive trans levels falls slightly below the equilibrium value. Correspondingly, the reactive product (cis) levels are fairly close to their equilibrium value, whereas the low energy product levels are obviously much less populated than at equilibrium. There is thus a pronounced inversion in the product, which could be used for laser action.

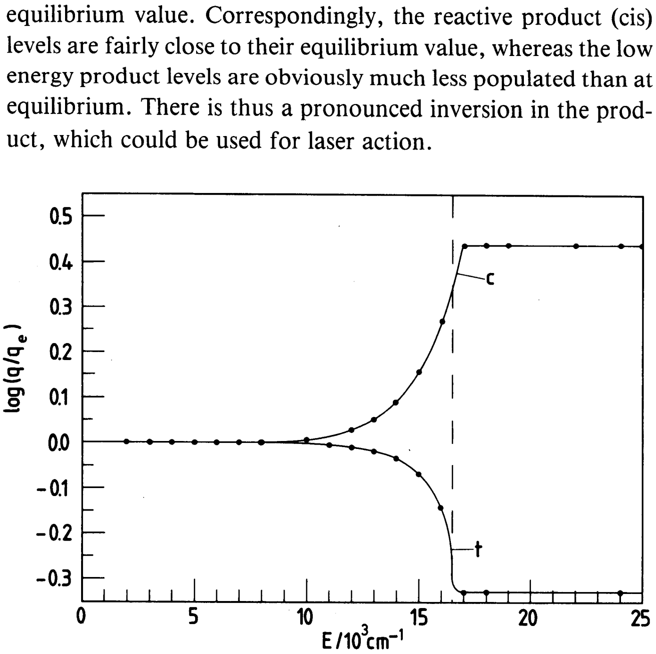

Fig. 8
Relative level populations q/q_e for the model reaction at 1200 K starting with pure trans at low pressures. The dashed line indicates the threshold energy E_T. See also the detailed discussion in the text

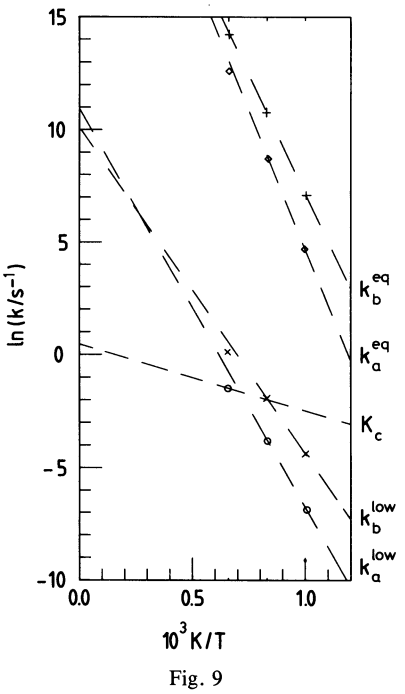

Fig. 9
Arrhenius diagram for the model reaction at low pressures. $\bar{k}^{\text{low}}$ are the apparent rate coefficients satisfying $\bar{k}_a^{\text{low}} + \bar{k}_b^{\text{low}} = k_r$. k^{eq} are equilibrium or high pressure rate coefficients. The dashed lines are only for visualization of the calculated points which do not show exact straight line behaviour. The dashed line marked K_C gives $\ln(k_a^{\text{eq}}/k_b^{\text{eq}})$

Fig. 8 gives an even more instructive insight in the origin of the fall-off of $k_r(\text{st})$.

There we have represented at steady state (and 1200 K, low pressures) the ratio of relative populations q/q_e for both cis and trans. This is a measure of the deviation from equilibrium considered for each isomer separately and can thus be directly related to the average k_a and k_b in Eq. (14). For the reactant (the trans isomer, labelled t) the low energy levels are essentially in Boltzmann equilibrium ($q_J = q_J^{\text{eq}}$), whereas the high energy levels have less than their equilibrium population. This is in qualitative agreement with the view of nonequilibrium theories of unimolecular reactions based upon the irreversible Lindemann mechanism and accounts for part of the fall-off (see Fig. 12 of Ref. [9]). However, even more pronounced is the overpopulation of reactive and further highly excited product states (cis levels, labelled c). As we have discussed in the previous section almost all of the fall-off is really due to this overpopulation, which creates a fast back reaction. The net relaxation rate coefficient is then slow, being the result of two opposing fast processes. Fig. 8 bears out the foundations of this particularly clearly in terms of the relative level populations q.

4. Measurement of the Canonical Rate Coefficient at Low Pressures

In order to complete our discussion of the model reaction, Fig. 9 shows an Arrhenius diagram for k_a^{eq}, k_b^{eq} and for the much lower apparent rate coefficients $\bar{k}_b^{\text{low}}$ and $\bar{k}_a^{\text{low}}$, which are computed from the measurable k_r using Eq. (19).

Fig. 9 indicates several known [11] effects, such as the slight deviations from linear Arrhenius behaviour for k^{eq} (with the Arrhenius parameters E_A^{eq} and A^{eq}). The curvature is somewhat larger at low pressures for $\bar{k}^{\text{low}}$, which has a much lower effective E_A^{low} and a low A^{low}. This low Arrhenius activation energy at the low pressure limit of thermal unimolecular reactions renders low pressure rate constants less suitable for the determination of activation energies considered as threshold energies for reaction. Also, the "high pressure" limiting rate constant k^{eq} contains the more relevant information about the intramolecular reaction dynamics. Therefore the k^{eq} are usually considered to be fundamental and desirable quantities to be determined. The usual procedure is, of course, to determine the pressure dependent apparent rate constants $\bar{k}$ from the measured relaxation k_r and extrapolate to high ("infinite") pressure in order to obtain k^{eq}, E_A^{eq} and A^{eq} for either reaction.

The most important result of the present paper is the proposal that this often ambiguous and difficult extrapolation procedure can be avoided altogether by measuring the true microscopic rate coefficients k_a^{eq} and k_b^{eq} at *low pressures and at equilibrium*. The direct observation of barrier crossings suggested in section 2 is experimentally quite difficult. At present, one will have to rely on indirect methods.

One such method is the analysis of spectroscopic line shapes in microscopically reactive systems at macroscopic thermal equilibrium. Such experiments are currently underway in our laboratory and we shall give only a rough outline of the basic idea here [15]. Consider a spectroscopic probe or chromophore attached to a molecule occurring in two isomeric forms A and B, giving chromophore absorption or emission at frequencies ν_A and ν_B. The chromophore can be a nucleus in a magnetic field, giving an NMR signal in the radiofrequency range [36, 37] or a bond with a localized vibration such as the CH-chromophore [38] absorbing in the IR or any other kind of chromophore in arbitrary frequency ranges. The chromophore plays the role of the "observer" for barrier crossings. If there is a fast reaction A $\rightleftarrows$ B the chromophore dynamics will be modulated, giving line broadening, coalescence and line narrowing as is well known from dynamic NMR spectroscopy [39] and has occasionally been suggested for use with IR [40] and Raman [41] spectroscopy. However, considerable care must be taken in the application to gas phase unimolecular reactions [42, 43]. At low pressures three different situations must be considered [15]:

1. Almost no reactive molecules above E_T are populated in thermal equilibrium and only nonreactive molecules below E_T are observed spectroscopically.

Then the line shape methods correspond essentially to a homogeneous situation; the measured rates are proportional to [M], being related to the ladder climbing processes similar to the relaxation coefficient k_r. The information is essentially equivalent to an ordinary relaxation experiment. There have been few investigations of this kind using NMR [42, 43].

2. An appreciable number of reactive molecules above E_T are spectroscopically observed. This corresponds to an inhomogeneous situation in which proper line shape analysis gives by averaging directly k_a^{eq} and k_b^{eq} which are *independent* of [M] (the spectrum will be dependent upon [M]).

3. Practically all molecules have an internal energy larger than the threshold energy E_T. The width of the internal energy distribution may be small compared to the mean energy (this may seem unusual to the reader but is in fact quite common, see for instance Ref. [38]). One has then an almost homogeneous situation (some corrections for the distribution should still be applied). The spectrum will be essentially independent of [M] and the analysis in terms of rate coefficients k^{eq} is straightforward. This is a special class of non-Lindemann reactions [15].

To our knowledge no previous analysis along these lines (2. and 3.) is available. However, our recent evaluation of inhomogeneous and homogeneous spectroscopic structures in IR-spectra in relation to intramolecular vibrational relaxation processes has paved the way for a similar analysis for intramolecular rearrangements [44]. Estimates show that the methods should certainly work with the use of IR-absorption but possibly also with NMR. The final result of such an experiment, in principle, will be the high pressure or canonical equilibrium rate coefficient without any extrapolation and independent of inert gas pressure even in the limit of zero pressure. This could be compared to the pressure dependent relaxation rate coefficients accessible via Eigen's *T*-jump technique [17], which G. Seyfang is currently implementing in our laboratory for gas phase reactions using pulsed TEA-CO_2-laser heating [45].

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