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Non-equilibrium rate coefficients and isotope effect with bimolecular ion-(polar) molecule reactions in xenon

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Using the Fokker-Planck version of an approximate Boltzmann equation for the ion (translational) energy distribution function f_I the departure, Δk, of the non-equilibrium ion-(polar) molecule reaction rate coefficient $k^{(\mathrm{non})}$ from its equilibrium value $k^{(\mathrm{eq})}$ is calculated. Δk enhances considerably with an increase of the dipole moment of the reacting molecular species ("locked dipole" reaction model). But the Δk-values, e.g. for reactions of $H^-(D^-)$ and nitromethane in xenon enhance also with increasing ratio ρ of the concentrations of CH_3NO_2 and Xe and decrease with enhancing gas temperature T. The reaction-induced (translational) non-equilibrium effect leads to a (non-equilibrium) kinetic isotope effect depending on ρ and T. At $T = 300$ K the example yields $k_H/k_D = 1.345$ $(\rho = 5 \cdot 10^{-4})$, $= 1.409$ $(\rho = 10^{-5})$ and $= 1.414 \simeq k_H^{(\mathrm{eq})}/k_D^{(\mathrm{eq})}$ $(\rho \leq 10^{-6})$.

Key words: Boltzmann equation — Dipole moment — Gases — Ions — Reaction kinetics

Basic relations

Let us assume a dilute inert carrier gas (C) of the temperature T in which the following components are dispersively distributed in small concentrations: ions (I) and reactive (polar) molecules M with concentrations in the following interrelation

$$n_I \ll n_M, n_C. \tag{1}$$

When in a gas a point ion (mass m_I, charge q_I, velocity $\boldsymbol{v}_I$) reacts with a polar molecule (mass m_M, polarizability α_M, permanent dipole moment μ_M, velocity $\boldsymbol{v}_M$) on the basis of electrostatic interaction potentials (induced and permanent dipole forces) then the energy-dependent cross section σ_R for a mutual capture of the reaction partners can be chosen as follows [1]:

$$\sigma_R = \sigma_L + \sigma_D = \sigma_{LD} \tag{2}$$

$$\sigma_L = \pi q_I (2\alpha_M)^{1/2} E^{-1/2} \tag{2a}$$

$$\sigma_D = \pi q_I \mu_M E^{-1} \tag{2b}$$

($E = (m/2)v^2$ kinetic energy of the relative motion of an ion-molecule pair, m its reduced mass, v relative velocity $|\boldsymbol{v}_I - \boldsymbol{v}_M|$). For non-polar molecules ($\mu_M = 0$) Eq. (2) leads to the Langevin-(Gioumousis-Stevenson) cross section $\sigma_R = \sigma_L \sim E^{-1/2}$. For polar molecules ($\mu_M \neq 0$) Eq. (2) gives the adiabatic "locked-dipole" approximation (LD) resulting in $\sigma_R = \sigma_{LD}$.

If the velocity (or translational energy) distribution functions f_I and f_M can be assumed to be the Maxwellians (i.e. translational equilibrium functions) $f_I^{(\mathrm{eq})}$ and $f_M^{(\mathrm{eq})}$, respectively, then an integration of $\sigma_R v$ (weighted with $f_I^{(\mathrm{eq})} \cdot f_M^{(\mathrm{eq})}$) over all the velocities $\boldsymbol{v}_I$ and $\boldsymbol{v}_M$ leads to

$$k^{(\mathrm{eq})}(T) = k_L^{(\mathrm{eq})} + k_D^{(\mathrm{eq})}(T) \tag{3}$$

$$k_L^{(\mathrm{eq})} = (2\pi q_I / m^{1/2}) \alpha_M^{1/2} \tag{3a}$$

$$k_D^{(\mathrm{eq})}(T) = (2\pi q_I / m^{1/2}) \mu_M (2/\pi k_B T)^{1/2}. \tag{3b}$$

Experiments with the flowing-afterglow and ICR-techniques have shown good agreement with the theory if the term in Eq. (3b) is multiplied by a "dipole locking constant" C lying between 0 (Langevin case, L) and 1 (locked dipole case, LD). Bowers and coworkers succeeded in calculating $C = C(\mu_M/\alpha_M^{1/2}, T)$, $0 < C < 1$ from a microscopic (statistical) point of view [2]. In the following we will use Eq. (3) ($C = 1$) for simplicity.

As is known from Prigogine and coworkers [3] the velocity (energy) distribution functions can be disturbed by the energetics of the proceeding reaction itself leading to non-equilibrium distribution functions $f_I^{(\mathrm{non})}$ and $f_M^{(\mathrm{non})}$ which result in a non-equilibrium rate coefficient $k^{(\mathrm{non})}$. The perturbation effect can be described generally by the departure Δk defined by

$$\Delta k = \left| \frac{k^{(\mathrm{non})} - k^{(\mathrm{eq})}}{k^{(\mathrm{eq})}} \right| \tag{4}$$

$$\begin{aligned} k^{(\mathrm{non})} &= (n_I n_M)^{-1} \int_3 \int_3 d\boldsymbol{v}_I \, d\boldsymbol{v}_M \, v \sigma_{LD}(v) f_I^{(\mathrm{non})}(\boldsymbol{v}_I) f_M^{(\mathrm{non})}(\boldsymbol{v}_M) \\ &= k_L^{(\mathrm{non})} + k_D^{(\mathrm{non})} \end{aligned} \tag{5}$$

$$k_L^{(\mathrm{non})} = (n_I n_M)^{-1} \int_3 \int_3 d\boldsymbol{v}_I \, d\boldsymbol{v}_M \, v\sigma_L(v) \, f_I^{(\mathrm{non})}(\boldsymbol{v}_I) f_M^{(\mathrm{non})}(\boldsymbol{v}_M)$$

$$= k_L^{(\mathrm{eq})} \tag{5a}$$

$$k_D^{(\mathrm{non})} = (n_I n_M)^{-1} \int_3 \int_3 d\boldsymbol{v}_I \, d\boldsymbol{v}_M \, v \, \sigma_D(v) f_I^{(\mathrm{non})}(\boldsymbol{v}_I) f_M^{(\mathrm{non})}(\boldsymbol{v}_M). \tag{5b}$$

In what follows $k^{(\mathrm{eq})}$-, $k^{(\mathrm{non})}$-, and Δk-values of ion-(polar) molecule reactions with a variation of the molecular property μ_M and the parameters T and $\rho = n_M / n_C$ will be investigated.

Boltzmann equation for $f_I^{(\mathrm{non})}$

Under the assumptions of Eq. (1) the change of the non-equilibrium distribution function $f_I^{(\mathrm{non})}(\boldsymbol{v}_I, t)$ in velocity $\boldsymbol{v}_I$ and time t can be described as follows

$$\frac{\partial f_I^{(\mathrm{non})}}{\partial t} = \left(\frac{\delta f_I}{\delta t}\right)_{IC}^{el} + \left(\frac{\delta f_I}{\delta t}\right)_{IM}^{R} \tag{6}$$

The first term (r.h.s.) of Eq. (6) is the collision integral of elastic IC-collisions which can be approximated for a mass ratio $m_I / m_C \ll 1$ by the differential expression:

$$\left(\frac{\delta f_I}{\delta t}\right)_{IC}^{el} = \frac{n_C m_I}{v_I^2 m_C} \frac{\partial}{\partial v_I}\left[v_I^3 \sigma(v_I) \left(\frac{k_B T}{m_I} \frac{\partial f_I^{(\mathrm{non})}}{\partial v_I} + v_I f_I^{(\mathrm{non})} \right)\right] \tag{7}$$

$\sigma(v_I)$ (elastic) cross section of elastic IC-collisions. The second term (r.h.s.) describes reactive IM-collisions:

$$\left(\frac{\delta f_I}{\delta t}\right)_{IM}^{R} = -n_M v_I \sigma_R(v_I) f_I^{(\mathrm{non})} \quad \text{if } |\boldsymbol{v}_I - \boldsymbol{v}_M| \sim v_I, \quad m_I / m_M \ll 1 \tag{8}$$

$$\sigma_R(v_I) = \sigma_{LD}\left(\frac{m}{2} v_I^2\right) \quad \text{according to Eq. (2)}$$

II-collisions are neglected because their frequency is much smaller than the frequencies of IC- and IM-collisions. It is assumed, too, that elastic CC-collisions - the most frequent kind of collisions - always maintain a Maxwellian distribution $f_C^{(\mathrm{eq})}(T)$. The same should be more or less true for the molecules:

$$f_M^{(\mathrm{non})}(T) \approx f_M^{(\mathrm{eq})}(T).$$

Equation (6) gives - in connection with Eqs. (7) and (8) - a partial differential equation (PDE) for $f_I^{(\mathrm{non})}(v_I, t)$. The initial distribution is assumed to be $f_I^{(\mathrm{non})}(v_I, 0) = f_I^{(\mathrm{eq})}(T_I(0) = T)$. The boundary conditions are $F_I^{(\mathrm{non})}(0, t) = F_I^{(\mathrm{non})}(\infty, t) = 0$ where $F^{(\mathrm{non})} \sim v_I^2 f_I^{(\mathrm{non})}$. The parabolic PDE can be solved by a suitable numerical method. Here we separated the variables v_I and t which leads to an eigenvalue problem. For steady-state investigations, which we are interested in, it is sufficient, however, to consider only the lowest eigenvalue. If we know $f_I^{(\text{non})}$ we can formulate the rate coefficients $k^{(\text{non})}$ and $k^{(\text{eq})}$ for ion-(polar) molecule reactions ($m_I \ll m_M$, m_C) as follows [4]:

$$\lim_{\tau\to\infty} k^{(\text{non})} = v_0 \int_0^\infty x\sigma_{LD}(x)P(x,\tau)\,dx \tag{9}$$

$$P(x,\tau) = F(x,\tau)n_I(0)/n_I(\tau) \qquad \int_0^\infty P(x,\tau)\,dx = 1$$

$$x = v/v_0, \qquad v_0 = (2k_BT/m_C)^{1/2}$$

$$\tau = t/t_0, \qquad t_0 = (n_C\delta_C v_0\sigma_0)^{-1}, \quad \delta_C = 2m_I/m_C, \qquad \sigma(x) = \sigma_0\bar{\sigma}(x)$$

$$k^{(\text{eq})} = (4/\pi^{1/2})v_0 \int_0^\infty \sigma_{LD}(x)x^3 \exp(-x^2)\,dx. \tag{10}$$

Results and discussion

1. Δk as a function of μ_M and T

In order to assess the maximum dipole-moment effect on Δk the *LD*-model according to Eq. (2) is used. In this case the quantity Δk from Eq. (4) can be split up into two factors:

$$\kappa_M = \frac{k_D^{(\text{eq})}}{k_L^{(\text{eq})} + k_D^{(\text{eq})}} = y(1+y)^{-1} \qquad y = \mu_M \Big/ \left(\frac{\pi}{2}\alpha_M k_B T\right)^{1/2} \tag{11}$$

and

$$\Delta k\{f_I^{(\text{non})}\} = \left|1 - \frac{k_D^{(\text{non})}\{f_I^{(\text{non})}\}}{k_D^{(\text{eq})}}\right|. \tag{12}$$

The factorization is possible because $k_{LD}^{(\text{non})} = k_L^{(\text{non})} + k_D^{(\text{non})}$ (cf. Eq. (5)) and $k_L^{(\text{non})} = k_L^{(\text{eq})}$. The latter is a singular property of the Langevin model (cf. [5, 6]).

The "equilibrium" quantity κ_M depends only on the data of the molecule $M(\alpha_M, \mu_M, T_M^R)$ where T_M^R is the rotational temperature of the molecule which for simplicity is always considered to be equal to T. For a homologous class of reactions between a fixed polar molecule and various ions the factor κ_M is a constant, Table 1 gives some κ_M-values at $T = 200$, 300, and 400 K.

Table 1. Factor κ_M for various molecules M

Molecule M				Factor	$\kappa_M(y)$	
	$\alpha_M \cdot 10^{24}$ in cm^3	μ_M in D	$\mu_M \cdot \alpha_M^{-1/2}$ in D $\cdot$ cm$^{-3/2}$	200 K	300 K	400 K
NH_3	2.26	1.47	0.98	0.82 (4.69)	0.79 (3.83)	0.77 (3.32)
CH_3CHO	4.40	2.69	1.28	0.86 (6.16)	0.83 (5.03)	0.81 (4.35)
CH_3NO_2	5.20	3.46	1.52	0.88 (7.28)	0.86 (5.95)	0.84 (5.15)
CH_3CN	4.56	3.92	1.84	0.90 (8.81)	0.88 (7.20)	0.86 (6.23)
HCN	2.59	2.98	1.85	0.90 (8.89)	0.88 (7.26)	0.86 (6.29)

The second factor, $\Delta k\{f_I^{(\text{non})}\}$ is a function of $f_I^{(\text{non})}$. According to Eqs. (7) and (8) the "non-equilibrium" quantity again depends on the properties of the molecular component (including n_M), but also on the parameters of the ions (q_I, m_I) and the carrier gas (m_C, n_C, $T_C = T$). Further $f_I^{(\text{non})}$ is affected by the elastic cross section $\sigma(x)$.

Figure 1 presents results of numerical Δk-calculations for a typical situation: $\alpha_M = 5.2\cdot 10^{-24}\,\text{cm}^3$, $m_I = m_{H^-}$, $m_C = m_{Xe}$ $\sigma = \text{const} = 40.1\cdot 10^{-16}\,\text{cm}^2$, $\rho = n_M/n_C = n_M/n_{Xe} = 10^{-3}$. As shown in Fig. 1, Δk increases with growing dipole moment μ_M which was varied between 0 and 4 D. A higher μ_M-value corresponds to a higher reactivity between H^- and M (cf. Eqs. (2) and (8)) leading to stronger deviations from the equilibrium distribution function $f_I^{(\text{eq})}$. Hence Δk has to increase with μ_M. Conversely a higher gas temperature T enhances the elastic collision term (6) which tends to bring $f_I^{(\text{non})}$ into the Maxwellian form $f_I^{(\text{eq})}$. Therefore the Δk-curves are lower for higher temperatures. At the point $\mu_M = 3.46$ D all the parameters coincide with the data for the reaction $H^- + CH_3NO_2$ in xenon. For this reaction Δk diminishes from 32.2% at 200 K via 22.3% (300 K) to 19.1% at 400 K ($\rho = 10^{-3}$).

In addition, in Fig. 1 is shown the "saturation curve" of the first factor κ_M (300 K) for CH_3NO_2 weakened by a factor 0.25. At $T = 300$ K the product $\Delta k = \kappa_M \cdot \Delta k\{f_H^{(\text{non})}\}$ has the factors $\kappa_M = 0.856$ and $\Delta k\{f_{H^-}^{(\text{non})}\} = 0.260$ ($\rho = 10^{-3}$).

2. *Δk as a function of $\rho = n_M/n_C$*

$(H^- + CH_3NO_2 \rightarrow CH_2NO_2^- + H_2)$

Figure 2 presents Δk-curves for the proton transfer reaction mentioned above as a function of $\rho = n_M/n_C$ at different temperatures. It appears from Fig. 2 that the non-equilibrium departure increases considerably as the number density ratio ρ rises. For ρ below 10^{-6} Δk is virtually vanishing. In this density region the "reactivity term", Eq. (8), cannot compete with the elastic collision term, Eq. (7), drawing $f_{H^-}^{(\text{non})}$ to $f_{H^-}^{(\text{eq})}$. With increasing ρ (i.e. with growing n_M at

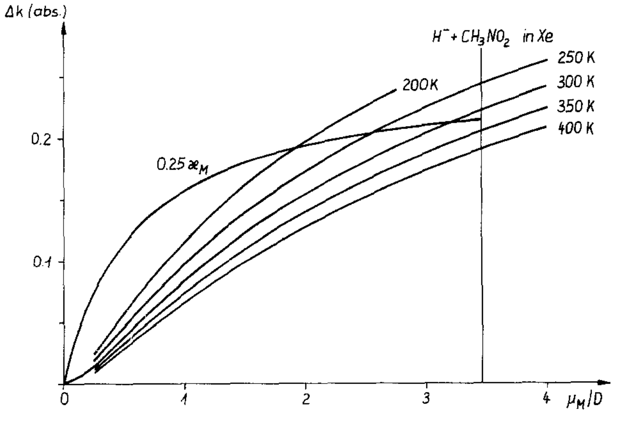

Fig. 1. Non-equilibrium departure Δk (abs.) as a function of μ_M

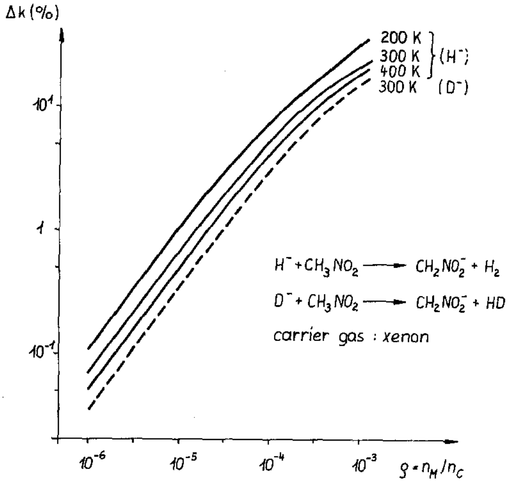

Fig. 2. Δk (%) as a function of the density ratio $n(CH_3NO_2)/n(Xe)$

fixed n_C) term (8) prevails more and more over term (7). Hence Δk is already some per cent if ρ lies between 10^{-5} and 10^{-4}. For $\rho \geq 5 \cdot 10^{-4}$ the non-equilibrium effects should not be ignored. The explanation of the temperature effects is the same as with Fig. 1.

3. Concentration-dependent kinetic isotope effect:

$$H^-(D^-) + CH_3NO_2 \xrightarrow{k_H(k_D)} CH_2NO_2^- + H_2(HD)$$

Let us regard the reaction of H^- and D^- ions with polar CH_3NO_2 molecules in xenon. The elastic collision term (7) contains the mass m_I explicitly. In the case of the H^- reaction the "reactivity term" (8) dominates the term (7) more than in the case of the D^- reaction. Thus the non-equilibrium deviations from $f_I^{(eq)}$ (and therefore from $k^{(eq)}$) will be stronger with the H^- reaction. That is the reason why for a fixed temperature the Δk-values of the H^- reaction are higher than in the D^- reaction as can be seen in Fig. 2 for $T = 300$ K.

Finally we want to investigate the ratio $k_H^{(non)}/k_D^{(non)}$ as a function of $\rho = n_M/n_C$. For a fixed concentration n_C of the carrier gas (xenon) the non-equilibrium effects will increase with enhancing concentration of the CH_3NO_2 molecules especially in the H^- reaction. Hence the ratio $k_H^{(non)}/k_D^{(non)}$ will decrease with growing ρ. Thus the kinetic isotope effect described by $k_H^{(non)}/k_D^{(non)}$ is concentration-dependent. For a very small ratio $\rho < 10^{-6}$, however, we have practically no non-equilibrium effect and therefore no dependence of k_H/k_D on the concentration, i.e. $k_H^{(non)}/k_D^{(non)}$ converges to $k_H^{(eq)}/k_D^{(eq)}$ which is illustrated in Fig. 3.

Mackay and Bohme made an experimental study of proton-transfer reactions in nitromethane at 297 K [7]. They found a value $k_H^{exp}/k_D^{exp} \approx 1.34$ for the $H^-(D^-)$-reactions. They used helium as carrier gas with a total pressure of 38.7 − 68.5 Pa. Unfortunately in helium the non-equilibrium effects are not so pronounced as in xenon. In addition it is impossible to approximate the elastic collision term

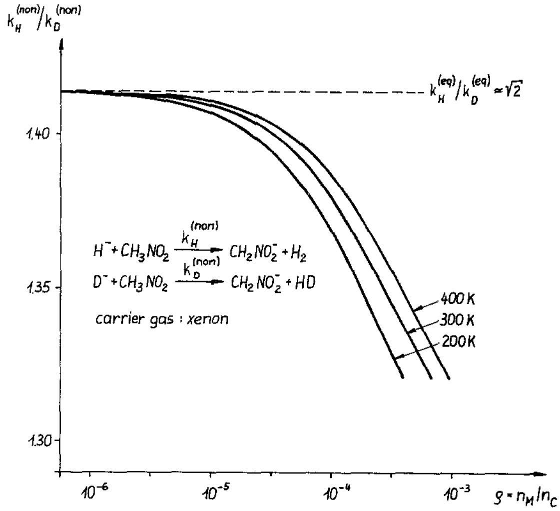

Fig. 3. $k_H^{(non)}/k_D^{(non)}$ as a function of $n(CH_2NO_2)/n(Xe)$

in the form (7) because the condition $m_I \ll m_C$ - which is necessary for the validity of (7) - is violated in the case of helium. Nevertheless it is interesting to note that also in the experiments $k_H^{exp}/k_D^{exp} \approx 1.34 < k_H^{(eq)}/k_D^{(eq)} \approx \sqrt{2}$.

Conclusion

Under the assumptions $m_I \ll m_M$, m_C and $n_I \ll n_M$, n_C a general expression for the non-equilibrium departure Δk has been derived. Numerical Δk-values can be obtained if the (translational) non-equilibrium distribution function $f_I^{(non)}$ of the ions is known which can be determined via an eigenvalue problem.

The kinetic quantity Δk has been calculated for ion- (polar) molecule reactions in a heavy carrier gas C in the framework of a locked-dipole approximation (LD). In this case the μ_M – dependence of Δk can be explained via two different factors, κ_M and $\Delta k\{f_I^{non}\}$; both of them increase with growing μ_M.

For the (anionic) proton-transfer reactions $H^-(D^-) + CH_3NO_2 \rightarrow CH_2NO_2^- + H_2(HD)$ the kinetic parameters $k_H^{(eq)}$, $k_D^{(eq)}$, $k_H^{(non)}$, $k_D^{(non)}$, and Δk have been estimated. Δk decreases with enhancing temperature T. The reaction-induced non-equilibrium behaviour of f_I and k leads theoretically to a concentration-dependent kinetic isotope effect $k_H^{(non)}/k_D^{(non)}$ in a heavy inert gas (xenon).

Some remarks should be added to the use of the locked-dipole model ($C = 1$) in relation to experiments. Like in all the other cases such a model will provide only an upper limit to dipole induced effects. Therefore the (non-equilibrium) isotope effect calculated here appears in its maximum form. This can be understood as follows: Changing from a kinetic situation in which the dipole locking "constant" $C = 1$ to the more realistic case $C < 1$ there is no variation in the equilibrium isotope effect:

$$k_H^{(eq)}/k_D^{(eq)}|_{C<1} = k_H^{(eq)}/k_D^{(eq)}|_{C=1}.$$

This equality comes from the fact that C is a function depending only on the properties of the molecule M. Therefore C remains constant at the transition from the (H^-, M)-reaction to the (D^-, M)-reaction, i.e. $k_H^{(\mathrm{eq})}/k_D^{(\mathrm{eq})} \approx (m_{D^-}/m_{H^-})^{1/2} \approx \sqrt{2}$. But in the case $C < 1$ the quantity $f_I^{(\mathrm{non})}$ is less far from $f_I^{(\mathrm{eq})}$ than in the case $C = 1$ with its stronger dipole effects. Therefore in Fig. 3 the concentration-dependent deviation of the curve $k_H^{(\mathrm{non})}/k_D^{(\mathrm{non})}$ from the (broken) line for $k_H^{(\mathrm{eq})}/k_D^{(\mathrm{eq})} \approx \sqrt{2}$ should be less pronounced than in the case $C = 1$. Nevertheless, it should be tried to measure the (reduced) isotope effect $(C < 1)$, because it offers the possibility of testing the phenomenon of a translational non-equilibrium effect (caused by the reaction) by variation of the concentrations n_M and n_C. By investigating the relative quantities k_H/k_D (and not the absolute k-values) it can be hoped that uncertainties in the choice of the reactive cross section for the (H^-, M)-reaction and its very similar counterpart of the (D^-, M)-reaction will cancel each other.

For an experimental verification of the isotope effect calculated (one-channel) proton transfer reactions $H^-, D^- + M$ should be preferred in which M is a polar molecule with a high dipole locking "constant" C, i.e. with larger ratios μ_M^2/α_M and diminished gas temperatures $T < 300$ K; the carrier gas should be xenon $(m_I/m_{Xe} \ll 1)$ and the ratio $\rho = n_M/n_{Xe}$ should be varied systematically between 10^{-6} and 10^{-3}.

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