

EFFECT OF MODE SEPARATION ON THE DECOMPOSITION RATE OF POLYATOMIC MOLECULES

Milan ŠOLC

*Institute of Inorganic Chemistry,
Czechoslovak Academy of Sciences, 160 00 Prague 6*

Received March 19th, 1985

A generalized equation for the unimolecular rate constant in the low-pressure region is used to estimate the effect of mode separation on decomposition rate. The controlling factor in determining the degree of ergodicity of the dynamics, and hence the decomposition rate, is the number of mode sets between which energy exchange is frozen. The distribution of modes within the sets is not crucial.

The theory of decomposition of highly vibrationally excited polyatomic molecules assumes intramolecular redistribution of the vibrational energy. The available data suggest that this redistribution occurs, at least between some degrees of freedom, on a time scale of the order of 10^{-10} to 10^{-12} s (see ref.¹). There have been speculations that the redistribution may be restricted to certain modes or sets of modes (*i.e.*, that the phase space of molecule is not completely ergodic²), for reasons of, *e.g.*, symmetry³ or the presence of a heavy atom separating two or more ligands in the molecule⁴. The existence in a molecule of sets of vibration modes within which a rapid redistribution occurs but between which there is only a restricted energy exchange is also assumed in theories of selective decomposition of laser-excited molecules^{5,6}. Some idea of the effect of mode separation on the decomposition rate may be obtained from values of the unimolecular rate constant in the low-pressure region, where the restriction on the energy redistribution has the most pronounced effect. A formula for the unimolecular rate constant of decomposition of a molecule with modes divided into sets was derived a long time ago^{7,8}, but has not, to my knowledge, been used to assess the effect of different types of mode separation on the decomposition rate.

The molecule is represented by n normal vibrations. These vibrations are divided into f sets, specified by the suffix $r = 1, \dots, f$; the r th set includes n_r modes. A rapid energy exchange is assumed between the members of the separate sets, while no such exchange is assumed between the separate sets. The parameters of the separate sets are given two suffixes, one denoting the set and the other the serial number of the mode within the set. The energies of the modes are $\varepsilon_{r,i}$, the frequencies $\nu_{r,i}$, where

$r = 1, \dots, f$ and $i = 1, \dots, n_r$. The vibration of the reaction coordinate $q(t)$ is given by a superposition of effectively normal modes,

$$q(t) = \sum_{r=1}^f \sum_{i=1}^{n_r} \alpha_{r,i} \varepsilon_{r,i}^{1/2} \cos 2\pi(\nu_{r,i}t + \psi_{r,i}), \quad (1)$$

where $\alpha_{r,i}$ are amplitude coefficients. The rate constant of the decomposition of molecules with the energies $\varepsilon_{r,i}$ is defined as the time-averaged number of passages of $q(t)$ over the critical value q_0 within a time unit. The model thus defined corresponds to Slater's model⁷. In the limit of low pressures, the generalized unimolecular rate constant derived for this model is of the form⁸

$$k \approx Z[M] (4\pi)^{(f-1)/2} (\varepsilon_0/k_B T)^{(2n-f-1)/2} \exp(-\varepsilon_0/k_B T) \cdot \prod_{r=1}^f \bar{\mu}_r^{2n_r-1} / \Gamma(n_r), \quad (2)$$

where

$$\bar{\mu}_r = \left(\sum_{i=1}^{n_r} \alpha_{r,i}^2 / \sum_{r=1}^f \sum_{i=1}^{n_r} \alpha_{r,i}^2 \right)^{1/2},$$

Z is the collision number, $[M]$ is the concentration of the inert gas which mediates the energy transfer in collisions, and ε_0 is the critical energy,

$$\varepsilon_0 = q_0^2 / \sum_{r=1}^f \sum_{i=1}^{n_r} \alpha_{r,i}^2.$$

Equation (2) provides a means for establishing how the value of k depends on the parameter f at qualitatively similar separations of modes into sets. The calculation is performed with the assumption that $\alpha_{r,i} = \alpha$ for all r, i . Table I gives values of the dimensionless quantity $\kappa = k/Z[M] \exp(-\varepsilon_0/k_B T)$ at different numbers of sets for the given division into sets with $n = 10$ and $\varepsilon_0/k_B T = 40$. It is seen that κ , and hence k , depends strongly on f , the value for a completely ergodic (RRKM) molecule ($f = 1$) differing from that for a molecule with no energy exchange ($f = 10$) by nearly two orders of magnitude. As the degree of ergodicity of the molecule decreases, so does the decomposition rate in the low-pressure region ($\log \kappa$ decreases in an approximately linear way with f).

Table II illustrates how the value of κ depends on the size of sets at fixed f . The results suggest that the set size is not crucial because, for example, the distributions 1-1-8 and 3-3-4 ($f = 3$) lead to κ -values that differ by no more than 10%. It may be stated, however, that the distributions 5-5 and 3-3-4 are "more ergodic" (have higher κ -values) than, respectively, the distributions 1-9 and 1-1-8.

TABLE I
Effect of the number of sets on decomposition rate

f	Distribution	$\kappa/10^7$
1	10	72.5
2	1-9	46.3
3	1-1-8	30.6
4	1-1-1-7	19.9
5	1-1-1-1-6	13.0
6	1-1-1-1-1-5	8.43
7	1-1-1-1-1-1-4	5.48
8	1-1-1-1-1-1-1-3	3.57
9	1-1-1-1-1-1-1-1-2	2.27
10	1-1-1-1-1-1-1-1-1-1	1.43

TABLE II
Effect of the set size on decomposition rate

f	Distribution	$\kappa/10^8$
2	1-9	4.63
2	2-8	4.88
2	3-7	4.95
2	4-6	4.97
2	5-5	4.98
3	1-1-8	3.06
3	3-3-4	3.36
4	1-1-1-7	1.99
4	2-2-3-3	2.24

It may be concluded that the decomposition rate, or the measure of ergodicity of the dynamics of molecules, depends on the number of separate sets of modes, but is virtually independent of the distribution of modes among the separate sets. This conclusion has been derived on the assumption that all $\alpha_{r,i}$ are equal. The factors that govern the separation of modes into sets may, however, affect the amplitude coefficients in such a way that some sets will not contribute to the vibration of the reaction coordinate $q(t)$. The calculation can then be made for an effectively smaller molecule, because some degrees of freedom will not represent an energy reservoir, nor will they affect the dynamics of $q(t)$.

REFERENCES

1. Oref I., Rabinovitch B. S.: *Accounts Chem. Res.* 12, 166 (1979).
2. Bloembergen N., Zewail A. H.: *J. Phys. Chem.* 88, 5459 (1984).
3. Laidler K. J., Wojciechowski B. W. in the book: *The Transition State*, p. 37. Chemical Society Special Publication No 16, London 1962.
4. Marcus R. A.: *Faraday Discuss. Chem. Soc.* 75, 103 (1983).
5. Thiele E., Goodman M. F., Stone J.: *Chem. Phys. Lett.* 69, 18 (1980).
6. Thiele E., Goodman M. F., Stone J.: *Opt. Eng.* 19, 10 (1980).
7. Slater N. B. in the book: *The Transition State*, p. 29. Chemical Society Special Publication No 16, London 1962.
8. Šolc M.: *Chem. Phys. Lett.* 1, 160 (1967).

Translated by M. Škubalová.