COMMENTS

Comment on the Possibility of Excited Recoil Energy Distributions in the Products of Complex-Forming Reactions with No Exit Barrier

L. Bonnet and J. C. Rayez*

Laboratoire de Physicochimie Moléculaire, URA 503 Université, Bordeaux 1 and CNRS 33405 Talence Cedex, France

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Since the studies of Polanyi and co-workers on the energy partitioning in the products of elementary chemical reactions,[1] it is often stated concerning complex-forming processes that a large average fraction $\langle F'_T \rangle$ *(≈50%) of energy released into product translation indicates the existence of a barrier in the exit channel.*[2,3] *This is often true, exit barriers leading to strong repulsions between nascent fragments such as in the case of the reaction CO + OH → CO₂ + H.*[4]

The goal of this Comment is to recall, however, that this statement, which is a rule rather than a principle, cannot be invoked systematically, particularly for triatomic systems. For instance, the processes Hg + I_2 → HgI + I,[5,6] Ba + O_2 → BaO + O,[7] C + NO → CN + O,[8] or O_2H → O_2 + H[9] lead to $\langle F'_T \rangle$ ≈ 60%, 55%, 55%, and 59%, respectively, although none of them involve an exit barrier along the reaction path.

To our knowledge, the first who had an inkling of the possibility of excited recoil energy distributions $P(F'_T)$ in complex-forming processes governed by attractive forces were Safron, Weinstein, Herschbach, and Tully.[10] They proposed an analytical expression of $P(F'_T)$ for reactions of the kind H + HH → HH + H or H + LH → HL + H (H and L are for heavy and light atoms, respectively) for which the product angular momentum L' is much larger in average than the product rotational angular momentum j'. Although such an expression could not account for $\langle F'_T \rangle$ larger than ≈40%, they proposed that *a shift of their distribution to higher energies could occur in sytems for which* (*i*) *the only channel for decay is the entrance channel or* (*ii*) *the asymptotic potentials and reduced masses of the entrance and exit channels are nearly the same*. This was indeed observed experimentally some years later by Bernstein et al. (Hg + I_2 → HgI + I)[5,6,11] and in simulated experiments by Morais and Varandas (Li + Li_2 → Li_2 + Li)[12] and the authors (inelastic collision model).[13]

Recently, we derived a simple expression for $P(F'_T)$, based on a model of partial treatment of angular momentum conservation (PAC).[14] Due to the simplicity of the PAC model, we could pinpoint the main factors that play a role in the dynamics of the processes considered above. The shift of $P(F'_T)$ toward high percentage evoked previously was clearly analyzed in terms of angular momentum constraints. It was also shown that another class of reactions without exit barrier for which $P(F'_T)$ is very excited is that of exothermic processes of the type H + HL → HHL → HH + L performed at very low collision energies; in such case, the reagent orbital angular momentum L is small so that only low values of j' are available with respect to the maximum one consistent with the product available energy E'. As a consequence, the rotational energy is small and a large part of E' may be channeled into the recoil motion. On the other hand, increasing the collision energy leads to a decrease of $\langle F'_T \rangle$ (see section VII in ref 14). Our feeling is that the reaction O(^{1}D) + IH → OI + H recently studied by Casavecchia et al.[3] could belong to such a class of processes; as a matter of fact, the exoergicity is equal to 30 kcal/mol, and at a collision energy E of 4.7 kcal/mol, $\langle F'_T \rangle$ = 55% whereas at E = 13.6 kcal/mol, $\langle F'_T \rangle$ = 46%.

To show that these percentages are consistent with a barrierless process, we have performed statistical calculations, using the method presented in ref 13 (see eq 24) which is a classical version of phase space theory devoted to product state distributions. The fluxes $F_\alpha(\mathbf{J},E)$ and $F_\beta(\mathbf{J},E'')$ are neglected with respect to $F_\gamma(\mathbf{J},E')$ since much more ro-vibrational levels are available in channel γ than in channels α and β. We have also neglected E'_V with respect to D' in eq 16. The parameters used are m_O = 16 amu, m_I = 127 amu, m_H = 1 amu, C_6 = 30 eV. Å^6,[15] and r'_e = 1.8 Å. Moreover, the polarizabilities of OI and H are sufficiently low for the dispersion force between OI and H to be negligible. As a consequence, the exit-channel dynamics are expected to be governed by a short-range force that we assume strongly attractive for $R \le R^‡$ and negligible for $R > R^‡$.[16] Any value of $R^‡$ between 2.5 and 3 Å being reasonnable, we keep $R^‡$ at 2.7 Å. $R^‡$ is also the maximum value of the exit-impact parameter so that $b'_M(E'_T)$ is replaced by $R^‡$ in eq 17 (see ref 13). The calculations lead to $\langle F'_T \rangle$ = 54% for E of 4.7 kcal/mol and $\langle F'_T \rangle$ = 47.6% for E = 13.6 kcal/mol, in good agreement with the results of Casavecchia et al.[3] Of course, these results do not allow for an eventual settlement of the existence or not of an exit barrier. They show, however, that an excited recoil energy distribution and its shift toward low energies when the collision energy increases are consistent with the assumption of no-exit barrier.

In conclusion, large fractions of energy released into translation in the products of complex-forming triatomic reactions without exit barrier are expected due to angular momentum constraints when (i) the reduced masses and the available energies are roughly the same in the entrance and exit channels or (ii) the product atom is much lighter than those of the product diatomic and the available energy in the reagents is much lower than in the products. When these two situations are encountered, it is difficult to attribute the excited nature of the translational energy distribution to an exit barrier without further information such as accurate quantum mechanical calculations of the potential energy along the exit reaction path.

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References and Notes

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