

## Chemical Kinetics and Hot Atom Chemistry – Present Status and Future Perspectives<sup>†</sup>

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### Abstract

Alice: "Would you tell me, please, which way I ought to go from here?"

Cheshire Cat: "That depends a good deal on where you want to get to."

### Introduction<sup>1</sup>

A field that has been the subject of ten international symposia may be said to have achieved maturity. Its practitioners should be able to evaluate what they can do well, and where their efforts are needed. In this paper progress is assessed in two areas of research in which the authors are deeply involved: the role of recoil atoms in chemical kinetics, and mechanistic studies with polyvalent recoil atoms. Some possible future directions are suggested. However, this exercise has been undertaken not to test our predictive abilities, but as a reminder that important tasks remain to be accomplished.

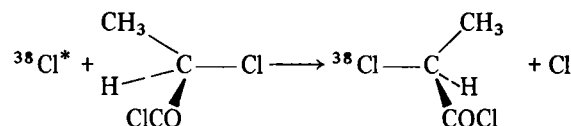
There are significant mechanistic differences between the reactions of monovalent recoil atoms, species whose valence is saturated by the formation of one covalent bond, and those of divalent and polyvalent atoms. These distinctions are illustrated in Table 1 for mono- and divalent species. Monovalent recoil atoms undergo relatively few types of reactions with covalently bonded substrate molecules. Most of these lead to the formation of stable pro-

ducts whose atoms exhibit normal valency. Even the free radical products obtained from addition, or from hot displacement followed by bond cleavage, can usually be efficiently converted into stable molecules through the use of appropriate scavengers. Thus the mechanistic questions about energetic monovalent recoil atoms have for many years centered on the detailed dynamics of reaction and on the energy dependence of the reaction probability [1–8]. For divalent species there often are competing reaction channels and the chances are much greater for formation of short-lived reactive intermediates, transient species that frequently exhibit unusual chemical behavior.

### Discussion

#### 1. Use of monovalent recoil atoms in non-equilibrium kinetics experiments

An exciting new perspective on the dynamics of hot substitution reactions by monovalent atoms has emerged from recent stereochemical studies. Greater than 80% *inversion* has been observed when high energy <sup>38</sup>Cl and <sup>34m</sup>Cl atoms replace a covalently bonded chlorine at the chiral center of 2-chloropropionyl chloride at gas-phase pressures of 0.5–0.8 atm [9].



Here the asterisk indicates that the recoiling <sup>38</sup>Cl atoms are translationally excited. These findings contrast with previous stereochemical studies in which observations of retention of configuration accompanying recoil tritium-for-hydrogen (T-for-H) atomic substitution [10–15] have been interpreted within the context of a 3-center direct, or "impact" [3, 4], reaction model.<sup>2</sup> Although evidence has also been available for many years supporting the occurrence of inverting hot T-for-H and Cl-for-Cl reaction modes [16–27], the significance of the available gas phase results has often been challenged.

Table 1. Schematic representation of primary reactions of monovalent and divalent recoiling atoms<sup>a</sup>

i. Abstraction	$\text{A} + \text{X} - \text{Y} - \text{Z} \rightarrow \text{A} - \text{X} + \cdot\text{Y} - \text{Z}$
ii. Displacement	$\text{A} + \text{X} - \text{Y} - \text{Z} \rightarrow \text{A} - \text{Y} - \text{Z} + \text{X}\cdot$
iii. Displacement with bond cleavage	$\text{A} + \text{X} - \text{Y} - \text{Z} \rightarrow \text{A} - \text{Y}\cdot + \text{X}\cdot + \text{Z}\cdot$
iv. Addition	$\text{A} + \text{W} = \text{Y} \rightarrow \text{A} - \text{W} - \text{Y}\cdot$
v. Insertion	$\text{B} + \text{X} - \text{Y} - \text{Z} \rightarrow \text{X} - \text{B} - \text{Y} - \text{Z}$
vi. Addition	$\text{B} + \text{W} = \text{Y} \rightarrow \begin{array}{c} \text{B} \\ \diagdown \quad \diagup \\ \text{W} \quad \text{Y} \end{array}$
vii. Abstraction	$\text{B} + \text{X} - \text{Y} - \text{Z} \rightarrow \cdot\text{B} - \text{X} + \cdot\text{Y} - \text{Z}$
viii. Displacement	$\text{B} + \text{X} - \text{Y} - \text{Z} \rightarrow \cdot\text{B} - \text{Y} - \text{Z} + \text{X}\cdot$
ix. Insertion with bond cleavage	$\text{B} + \text{X} - \text{Y} - \text{Z} \rightarrow \text{X} - \text{B} - \text{Y}\cdot + \text{Z}\cdot$

<sup>a</sup> Taken from GASPAR, P. P., MARKUSCH, P., HOLTON III, J. D., FROST, J. J.: *J. Physic. Chem.* 76, 1352–1365 (1972). A denotes a monovalent atom and B a divalent atom. Stable products are shown in boldface type.

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1. This paper was first presented as a plenary lecture on September 7, 1979, at the 10th International Hot Atom Chemistry Symposium, Loughborough University of Technology.
2. The n-centered designation specifies the number of atoms whose motions are strongly perturbed during the substitution process.