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Existence of Negative Activation Energies in Simple Bimolecular Metathesis Reactions and Some Observations on Too-Fast Reactions

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A large number of reactions of the type $R^{\bullet} + HX$ and $R^{\bullet} + X_2$ have been reported as having negative activation energies ($X = I, Br, Cl$). These reactions have none of the behavior of reactions that are expected to have negative activation energies. It is shown that they must be simple metathesis reactions having a single transition state, $(R\cdot H\cdot \dot{X})^{\ddagger}$ or $(R\cdot X\cdot \dot{X})^{\ddagger}$. It is concluded that the negative activation energies must be artifacts of the experimental techniques employed. Some of what appear to be simple metathesis reactions but which proceed via atom + radical recombination have had rate constants reported, close to the collision limit. When examined from a collisional point of view, it is shown that they require collision diameters from 8 to 25 Å, far in excess of any known long-range interaction at these distances between neutral species. Again, artifacts of the experimental methods may be responsible.

Introduction

Exothermic reactions between free radicals (and/or atoms) and molecules have, since their extensive study which started about 1934, been characterized by small but positive activation energies in the range from 1 to about 12 kcal/mol. It therefore came as somewhat of a surprise when, about 10 years ago, reports began to appear suggesting that some of these had negative activation energies. Most of the ones reported were of the type $R + HX \rightarrow RH + X$ and $R + X_2 \rightarrow RX + X$ where R could be alkyl or substituted alkyl radicals and X was Br or I. A number of the R + HX are listed in Table 1, while $R + X_2$ are shown in Table 2.

There are a number of bimolecular, metathesis reactions that are expected to have negative activation energies. These fall into the general category of reactions that proceed over a potential well.[10−14] These have been discussed and have a number of verifiable features, as follows.

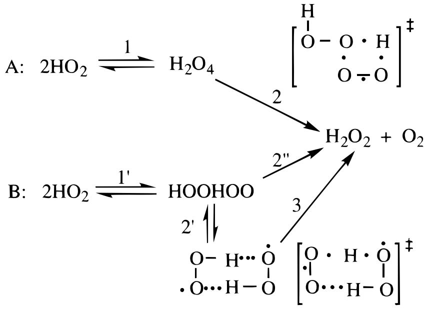
1. They involve two or more steps with two or more intervening transition states, where the first step is actually the formation of a weakly bound complex (chemical activation step).
2. The second (usually a tight or cyclic) transition state has a barrier ($V_2^{\ddagger}$) below the first transition state, so that $V_1^{\ddagger} > V_2^{\ddagger}$, when only two are involved.
3. As a consequence of 2, the *A*-factor of the second transition state is significantly smaller than that for the reverse process.
4. They will be sensitive to pressure due to the possibility of collisional deexcitation of the first bound complex.
5. Deuterium isotope substitution increases the V_2 potential due to substantial zero-point energy correction, while the V_1 potential of the first step, complex formation, is practically insensitive to isotope composition. Consequently, they will show an inverse isotope effect, $k_H/k_D < 1$, and it will approach A_H/A_D with increasing temperature.
6. With increasing temperature, the vibrational energy contribution to V_2 potential becomes gradually significant. It causes convex curvative (to $1/T$ axis) of an Arrhenius plot even to the extent of changing the sign of E_a.

Reaction with Negative Activation Energies

A typical example of a complex metathesis is provided by the reaction of two $HO_2^{\bullet}$ radicals:[13]

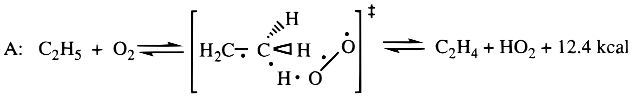
$$2HO_2^{\bullet} \rightarrow H_2O_2 + O_2$$

This reaction can proceed via two independent pathways:



The sole intermediate formed in path A, H_2O_4, has a 10 kcal central O−O bond. In path B step 1′ produces a H-bonded open dimer worth about 7 kcal, while the cyclic dimer formed in step 2′ is in a 14 kcal well. Path B seems to fit the data better. The negative activation energy for the overall reaction is −1.0 ± 0.5 kcal[14] over the range 220−700 K. Reflecting the tight transition state, the *A*-factor is low. At 1 atm it is 6×10^{-13} cm^3/(molecule s). Pressure effects have been observed.

Another example, even more complex, of a polystep metathesis is provided by the very important reaction of O_2 with alkyl radicals. Choosing ethyl for our example, we can have a direct metathesis with a single transition state:



and a complex path with two stable intermediates:

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TABLE 1: Some Metathesis Reactions of the Type $R^{\bullet} + HX$ with Negative Activation Energies

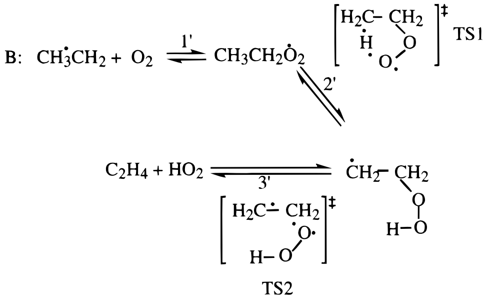
reactants	10^{12} *A*, cm^3/(molecule s)	E_{act}, kcal/mol	ref
CH_3/HCl	0.50 ± .07	+1.4 ± 0.3	1
	0.25 ± .02	+0.75 ± 0.2	2
CH_3/HBr	1.57 ± 0.26[a]	−0.38 ± 0.14	3
	1.36 ± 0.10	−0.46 ± 0.046	4
	0.80 ± 0.30	+0.95	40, 38
	0.68	+0.8	5, 41
CH_3/DBr	1.07 ± 0.17	−0.26 ± 0.11	4
CH_3/HI	4.5 ± 0.8[a]	−0.29 ± 0.14	5
CF_3/HI	0.90	0.5 + 0.5	39
C_2H_5/HBr	1.70 ± 0.55	−1.00 ± 0.29	3
	1.33 ± 0.33	−1.07 ± 0.16	4
	1.43 ± 0.9	+0.44 ± 0.03	6
C_2H_5/HI	4.5 ± 0.9	−0.77 ± 0.14	5
i-C_3H_7/HBr	1.58 ± 0.38	−1.53 ± 0.22	3
	1.33 ± 0.33	−1.07 ± 0.16	4
i-C_3H_7/HI	3.9 ± 0.8	−1.22 ± 0.17	5
t-C_4H_9/HBr	1.37 ± 0.5	−1.86 ± 0.34	3
	1.07 ± 0.3	−1.91 ± 0.30	4
t-C_4H_9/HI	3.1 ± 0.6	−1.51 ± 0.19	5

[a] A value of 1.0×10^{-12} is calculated for a tight TS with C−H−Br collinear. A similar value is for Me + HI.

TABLE 2: Some Metathesis Reactions of the Type $R^{\bullet} + X_2$ with Negative Activation Energies

reactants	10^{12}*A*, cm^3/(molecule s)	E_{act}, kcal/mol	ref
CH_3/Cl_2	5.0 ± 1.2	+0.53 ± 0.12	7
	18	+1.7	8, 37[c]
	13	+2.3	46
	20	+2.2	47
CH_3/Br_2	20 ± 4	−0.39 ± 0.25	8
	96[d]	[−0.38][d]	3, 37
CH_3/I_2	6.0 ± 2.4	0 (assumed)	38
CF_3/I_2	4.3	0 ± 0.5	39
C_2H_5/Cl_2	13 ± 3	−0.30 ±0.11	7
	7.7 ± 1.6[b]	[0][b]	24
C_2H_5/Br_2	26 ± 8	−0.82 ± 0.41	8
	8.5	0.44	6, 36
	10.0	−1.00	3, 36
C_2H_5/I_2	6.3 ± 2.4	[0] assumed	38
i-C_3H_7/Cl_2	25 ± 6	−0.49 ± 0.23	7
i-C_3H_7/Br_2	24 ± 7	−1.07 ± 0.45	8
t-C_4H_9/Cl_2	40 ± 9	0.0 ± 0.14	7
t-C_4H_9/Br_2	20 ± 6	−0.97 ± 0.45	8
t-C_4H_9/I_2	1.2 ± 3	[−2.9][a]	5, 9

[a] In ref 9 the ratio of *k*(t-Bu + HI)/*k*(t-Bu + I_2) was measured near 500 K as 0.25 with a positive activation energy of 1.4 ± 0.5 kcal. These numbers are used with results from ref 5 to obtain the values shown. [b] This is the rate constant at room temperature, assuming zero activation energy. [c] Calculated from relative measurement of $k(CH_3 + Cl_2)/k(CH_3 + Br_2)$ together with use of $k(CH_3 + Br_2)$ from ref 8. [d] Calculated using ref 30 for the ratio of $k(CH_3 + Br_2)/k(CH_3 + HBr)$ and parameters of reference 3 for the latter.



Direct metathesis A is expected to have a normal activation energy of about 5 ± 1 kcal/mol, while path B has been reported to have a negative activation energy of about −5 kcal/mol.[14] In the B path, step 2′, the isomerization of $EtO_2^{\bullet}$ to $\dot{C}_2H_4O_2H$, is rate determining ($k_3' > k_{-2}'$), with an estimated energy of activation of about 27 kcal/mol and a low *A*-factor of about $10^{12.2}$ s^{-1}. Step 1′ is expected to be at equilibrium above 400 K at 100 torr so that the overall rate constant including 1′ is given by $K_1'k_2'$ with a combined *A*-factor of about 1.7×10^{-14} cm^3/(molecule s). Since the *A*-factor for the direct metathesis is expected to be about 3.3×10^{-12} cm^3/(molecule s), we find that at about 900 K the two paths are expected to be equal, while at 600 K the complex path B is about 20-fold faster.

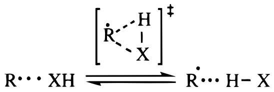
Let us now see what light these examples can bring to the metatheses of $R^{\bullet} + HX$ and $R^{\bullet} + X_2$.

Metatheses of R• with HX and X_2

It has been proposed that the metatheses of $R^{\bullet} + HX$ is a two-step process in which a weak complex R·X−H is first formed, which then isomerizes to R·H−X, which is a second complex preceding the second transition state[16]

$$[\mathrm{R{\cdot}H{\cdot}\dot{X}}]^{\ddagger} \rightarrow \mathrm{RH} + \mathrm{X}^{\bullet}$$

leading to final products. The first transition state (TS) is postulated as having a cyclic structure:



One may ask what role the first transition state plays since it does not itself lead to products. If it has a weak binding of $R^{\bullet}$ to the halogen atom in HX, this binding is totally lost in passing to the second TS. In such case what prevents the formation of this second TS directly?

Transition-state theory is an "equilibrium" theory in that the TS is in equilibrium with reactants. With the first TS in equilibrium with [R·H−X] and this latter in equilibrium with $R^{\bullet}$ + H−X, the second TS is also in equilibrium with $R^{\bullet}$ + H−X, and so the first transition state plays no role. Only the second TS determines the reaction rate. This is very different from the $R^{\bullet} + O_2$ examples shown where totally different chemical species and different steps are rate determining. In fact the formation of the first structure, R·X−H in which the $C^{\bullet}$ atom in $R^{\bullet}$ is in contact with the halogen of HX, is guaranteed to prevent formation of final product RH. If X is, for example, an I atom, then the $\dot{C}$−X distance in the complex is anywhere from 3.9 Å (van der Waals contact) to 2.6 Å, corresponding to weak, half-bond formation. At any of these separations the closest C···H distance possible is from 4.2 Å (linear complex) to 3.1 Å (I−H bond at 90° to C···I contact). Thus there is no energetic role possible for the C···I interaction in the final TS.

The first TS, shown as cyclic, has strong constraints on its formation. It cannot have even weak covalent character since the three electrons involved in the metathesis will then have a repulsive triplet interaction between two of them and in the cyclic structure this triplet pair must be found on one of the three atoms. Ion pair states such as R^+ $H-X^-$ or R^+ $X-X^-$ require too much energy to contribute to the reaction.

Bimolecular reactions with no barrier and the longest range interaction between neutral species, namely the valence interaction preceeding radical recombination which occurs at distances between 4 and 6 Å, show zero activation energies.[50] When modeled by the modified Gorin theory, they have a small positive $T^{1/6}$ temperature dependence, which has however never been confirmed experimentally. It is probably too small to measure with current limits of accuracy.

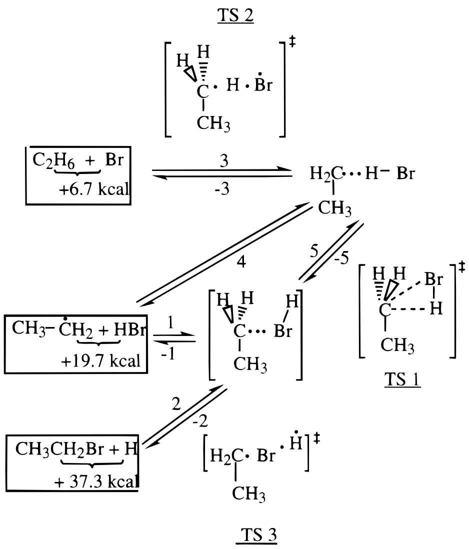


Figure 1. Reaction paths and transition states proposed for the reactions Br + C_2H_6, HBr + C_2H_5, and H + C_2H_5Br.

The conclusion from these considerations is that a weak van der Waals' interaction between $C^\bullet$ of the radical and X in the HX can play no role in the final metathesis. Only the $\geqslant C\cdot H{-}X$ structures can lead to observed products, and only the corresponding TS plays a role in the kinetics.

Some further light is shed on these arguments by considering the reaction of $R^\bullet$ with X_2. Here only one TS is possible, namely, $R\cdot X\cdot\dot{X}$. There is no plausible second complex or TS. These metatheses must proceed as normal metatheses. Yet if look at Table 2, we see that seven of them involving Cl_2 and Br_2 have been listed with negative activation energies.

A chemical observation is of interest. In the reactions of H atoms with R−X where X is I or Br the only products observed are $R^\bullet$ + HX, and all of these reactions have positive activation energies.[17−19,42] The transition states for these reactions are thus normal, direct metatheses.

$$[R\cdot X\cdot\dot{H}]^{\ddagger}$$

These TS correspond to the structures postulated for the weak complex 1, and we see that there is no tendency to transform them to the presumed, thermodynamically more stable, $R\cdot H\cdot\dot{X}$ despite the greater available energy in these systems. These observations are summarized in Figure 1 for the particular cases of C_2H_5 + HBr, C_2H_5Br + H, and C_2H_6 + Br.

We have recently measured the rates of reaction of C_2H_5 + HBr over the range 228−368 K using the techniques of very low pressure reactor (VLPR).[6] We have found a quite normal reaction rate with a positive activation energy of 444 ± 26 cal/mol, in contrast to the values of −1004 ± 287 and −1071 ± 155 listed in Table 1. Even more striking is the fact that at 298 K our observed value of the rate constant is about 14-fold smaller than the values in Table 1. We will comment further on this later.

All three reactions can occur without utilizing TS 1, and the products of reaction 2 show that path 5 in Figure 1 plays no role in this system.

It is instructive to trace the reaction backward. In Figure 2 we have drawn, approximately to scale, the tight transition state for the C_2H_5 + HBr reaction. In order to produce products C_2H_6 + Br, the two reactants must pass through the geometry shown by this transition state. The outlines shown as circles around the atoms Br and H represent van der Waals radii. In the geometry shown, the Br atom has no room in which to move to be closer to the $C^\bullet$ of the ethyl radical. The intermediate H atom being transferred effectively fills the space about the $C^\bullet$ radical. Even if we move the H atom back by 1.5 Å in the geometry of a contact transition state between $C^\bullet$ and H, the Br atom is also pushed 1.5 Å away, and it will make contact with the H atoms on the C_2H_5 radical before it can make contact with the $C^\bullet$.

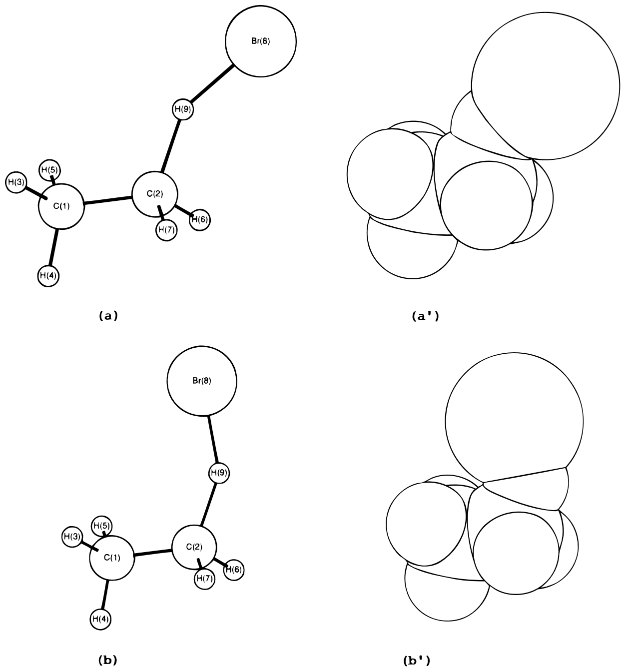


Figure 2. Tight transition state for reaction of C_2H_5 with HBr. (a) and (b) are ball and stick models showing trans (a) and cis (b) geometries of Br relative to the CH_3 group. (a′) and (b′) are space-filling models of the same structures showing van der Waals' radii.

Scanning the reported *A*-factors in Table 1, we see no example of an abnormally low *A*-factor such as might be expected for a two-step mechanism involving two intermediates with two transition states, one of them with a low-entropy, cylic structure. (Contrast this with the low *A*-factor for $C_2H_5 + O_2$.) In fact the *A*-factors range from 0.3 × 10^{-12} to 5 × 10^{-12} cm^3/(molecule s) with no consistent variation with X from Cl to Br to I or with R from Me to t-Bu. This variation instead may be interpreted as a measure of systematic biases in the experimental methods used.

Of particular interest are the four values listed in Table 1 for the reaction CH_3 + HBr. The *A*-values span a small range of about a factor of 2. However two values of E_{act} are negative, while two are positive. Both the latter are composites obtained from independent sets of measurements. Reference 40 is a relative measurement of CH_3 + HBr with $CH_3 + I_2$, while ref 38 is an absolute measurement near 300 K of $CH_3 + I_2$. This value derived from the two is in excellent agreement (2%) with the absolute value of $k(CH_3 + HBr)$ at 300 K derived from ref 41 and ref 5. Reference 41 is a relative measurement of $k(CH_3 + HBr)$ with $k(CH_3 + HI)$ combined with data of ref 5 for the latter. The reactions with negative activation energies (CH_3 + HBr) are about 4-fold faster than those with positive activation energies at 300 K.

A similar range is seen in the reactions of R + X_2 (Table 2), where $10^{-12}A$ varies from 5−40 cm^3/(molecule s). Again there is no correlation with X (Cl, Br, I) or with alkyl R (Me, Et, i-Pr or t-Bu). A mean value of (20 ± 15) × 10^{-12} cm^3/(molecule

s) characterizes most of these values and again might be taken as a measure of the range of systematic effects in the experiments.

One of the reactions listed in Table 2 between $Cl_2 + CH_3$ has a positive activation energy and thus presumably a normal *A*-factor, namely 5×10^{-12} cm^3/(molecule s). In striking contrast the reaction between C_2H_5 and Cl_2, which has a negative activation energy, has an *A*-factor 4-fold larger, 20×10^{-12} cm^3/(molecule s). We would expect the *A*-factor for $Et + Cl_2$ to be smaller than that for $Me + Cl_2$ if they both go by a direct metatheses route since the overall reaction has about a 3 eu or more, negative entropy change for $Et + Cl_2 \rightarrow EtCl + Cl$ than for $Me + Cl_2 \rightarrow MeCl + Cl$.[20] A simple, normal, tight nonlinear transition state[20] for both Me and Et gives about 6×10^{-12} cm^3/(molecule s) for the *A*-factors. This agrees with the value for $CH_3 + Cl_2$ in Table 2 but is 2-fold smaller than that for $Et + Cl_2$, which is however within the uncertainty of the methods used.

Two of the studies on $CH_3 + Cl_2$ were done by classical methods.[46,47] One was a steady state photolysis[46] of $Cl_2 + CH_4$ mixtures in which C_2H_6 was one of the termination products. The observed 3/2 order in Cl_2 verifies termination by $2CH_3 \rightarrow C_2H_6$ as the major termination and in principle permits the slow step, $k(CH_3 + Cl_2)$, to be determined with good precision. As can be seen, the results are in good agreement with a flash photolysis study of $CH_4 + Cl_2$ in which CH_3 was followed by absorption spectroscopy, and in addition, the final products CH_3Cl and C_2H_6 were both measured directly. For obscure reasons, little subsequent work has paid much attention to these two studies.[48] Both are appreciably slower by a factor of 7 at 300 K than the flash photolysis study which followed only the methyl radical loss by mass spectroscopy.[7]

Reactions that might be expected to have negative activation energies by the reasoning of the flash photolysis workers are the reactions of $H + HI$ and $H + I_2$. Very recent studies[51] have shown that both of these have positive activation energies of 0.62 ± 0.20 kcal/mol and 0.41 ± 0.20 kcal/mol, respectively. The $H + I_2$ reaction is favored to form polar complexes at $H\cdots I{-}I$ distances on the order of 1.7 Å, due to the electron affinity of H atoms (0.7 eV) and the low ionization potential of I_2. The alkyl radicals which have electron affinities close to zero and larger contact distances cannot do this. Despite this, the $H + I_2$ reaction has a positive activation energy.

Ab initio calculations have been done on a number of these reactions using a variety of sophisticated programs.[52−55] These studies ruled out the $R\cdots X{-}H$ complex as playing any role. For the reaction of $CH_3 + HCl$ they showed[53] a weakly bound van der Waals complex (0.67 kcal/mol) at a $C\cdots H$ distance of 2.60 Å, which is close to the van der Waals contact distance of 2.95 ± 0.1 Å.[20] This is followed by a positive barrier of 2.53 kcal/mol, quite close to the measured value of 2.8 kcal/mol. For $CH_3\cdots H{-}Br$ they find a weaker complex (0.28 kcal/mol) at 2.67 Å followed by a positive barrier of 0.67 kcal/mol. In both cases the weak van der Waals binding is below a positive barrier. This would appear to establish for both reactives a positive activation energy since *all* chemical metatheses proceed through a weak van der Waal's complex. However the authors decided to fit the data of the flash photolysis workers for $CH_3 + HBr$ (see refs 3 and 4 for earlier work). They did this by lowering their calculated barrier by 0.78 kcal/mol to a small negative barrier of −0.28 kcal/mol! They justified this on the grounds of the intrinsic uncertainty of their calculation being about 2 kcal/mol. But even this was not enough. In a second paper[54] they added an Eckert tunneling correction in an effort to fit the data. Tunneling has of course a negative activation energy. Since the "revised" barrier is now only 0.17 kcal above the van der Waals barrier and the total energy in the complex is about 3*RT* (1.8 kcal at 300 K) from translation and rotation, it is difficult to understand the role that tunneling can play.

TABLE 3: Bimolecular Rate Constants with Large Collision Diameters. Atom and Molecule

reaction	$10^{11}k_{298}$, cm^3/(molecule s)	$g^{\ddagger}_{el}$	α_1/α_2	σ_c, Å	ref
$Cl + C_2H_6 \rightarrow$	6.1	1/2	1/1	2.5	32
$HCl + C_2H_5$	(44)[a]			(5.1)[a]	calc
$F + CH_4 \rightarrow$	6.6	1/2	1/1	2.4	21
$HF + CH_3$	(32)[d]			(3.8)[d]	calc
$F + CH_3I \rightarrow$	17[c]	1/2	1/1	4.0	21
$\{$ $IF + CH_3$[c]	10				
$HF + CH_2I$	7				
	50[e]				calc
$Cl + C_2H_4 \rightarrow$	30 (k_∞)[b]	1/2	1/0.5	8	22
C_2H_4Cl (k_∞)					
$Cl + CH_2CO \rightarrow$	25	1/2	1/0.5	7.0	23
$CH_2Cl + CO$					

[a] Calculated assuming C_2H_6 can be viewed as a cylinder of radius 3.8 Å and length 8.8 Å. [b] This is the bimolecular rate constant extrapolated to infinite pressure. [c] The Path leading to $IF + CH_3$ is about 1.5 faster than that leading to HF plus CH_2I. [d] Calculated assuming that every collision of F with CH_4 with a collision diameter of 3.8 Å leads to reaction. [e] Calculated assuming that every collision of F with CH_3I leads to reaction. CH_3I is assumed to be a cylinder of radius 3.8 Å and length 9.7 Å.

The third paper in the series[55] examines among others the $C_2H_5 + HBr$ reaction but with a lesser degree of sophistication. This showed no van der Waals interaction, so there is only one barrier. However this barrier is calculated to be −0.85 kcal/mol. It is very difficult to visualize a single negative barrier to an exothermic reaction, and we shall not comment further. However even with this value and tunneling corrections they still fall short by a factor of 4 in fitting the experimental data.[3]

Reactions That Are Too Fast

Along with the category of simple metathesis reactions having negative activation energies is a category of bimolecular reactions we will call "too fast". Again, over about the same time frame, the past 15 years, these reactions have been appearing in the literature. What characterizes these reactions?

They all have bimolecular rate constants at or near the collision limit, loosely defined as 3×10^{-10} molecules/(cm^3 s). This would be the value for a collision diameter of 4.0 Å of spherical particles at 300 K with a reduced mass of about 15 amu. A number of such rate constants are listed in Tables 3 and 4.

Why are these reactions of concern since only one or two at most seem to be above the 4.0 Å collision diameter rate? The answer is that they are not spherical particles, and there are strong constraints both geometrical and electronic on the number of collisions that can lead to reaction. We shall show that when these constraints are included in the collision rate, the permitted rates require abnormally large collision diameters.

Table 3 is a compilation for some atom-molecule reactions, whereas Table 4 is a list of some atom−radical reactions, all of which appear to go by an addition mechanism to form a vibrationally excited species which then dissociates to final products. Table 3 is composed of two different sets of mechanisms. The first four examples are simple, direct atom−molecule bimolecular metatheses, while the last two represent

TABLE 4: Bimolecular Rate Constants with Large Collision Diameters. Atom + Radical Additions

reaction	$10^{11}k_{298}$, cm^3/(molecule s)	$g_{el}^{\ddagger}$	α_1/α_2	σ_c, Å	ref
$Cl + C_2H_5 \rightarrow$	1.20	1/8	1/0.5	3.1	32
$HCl + C_2H_4$	[2.7][a]			[5.4][a]	calc
	24			15	24
	30			17	25
	29			17	26
$H + C_2H_5 \rightarrow$	6	1/4	1/0.5	2.5	44
$2CH_3$				(3.5)	
$Br + C_2H_5 \rightarrow$	1.18	1/8	1/0.5	3.1	6
$HBr + C_2H_4$					
$Cl + CH_3CO \rightarrow$	25	1/8	1/<0.5	>10	23
$HCl + CH_2CO$					
$H + CF_3 \rightarrow$	9.1[b]	1/4	1/0.5	3.0	27
$HF + CF_2$	8.9			3.0	28
				[3.5][a]	calc
$O + CH_3 \rightarrow$	14	1/7	1/0.5	8.4	29
$OH + CH_2$				[4.4][a]	calc
$O + C_2H_5 \rightarrow$	22	1/7	1/0.5	12.1	30
Products				[4.4][a]	calc
$O + t\text{-}C_4H_9 \rightarrow$	87[c]	1/7	1/0.5	25	31
Products				[4.4][a]	calc

[a] Calculated from modified Gorin model.[32] [b] This rate constant was mistakenly reported in ref 25 as 9.1×10^{-10} cm^3/(molecule s). [c] This rate constant was described as “extraordinarily large” in ref 43.

a more complex mechanism in which addition of the atom to a double bond in the molecule is rate limiting.

In Table 3 the reactions of $Cl + C_2H_6$, $F + CH_4$, and $F + CH_3I$ have relatively fast rate constants, but all are appreciably smaller than the collision frequency, as evidenced by the values listed for the collision diameters (column 5, Table 3) calculated from the observed rate constants, the electronic partition formation g_{el}, and the van der Waals collision rates. For $Cl + C_2H_6$, the van der Waals collision rate is 44×10^{-11} cm^3/(molecule s) (column 2, Table 3) compared with the observed rate constant of $6.1 \times 10^{-11} cm^3$/(molecule s). Thus the observed rate constants for these three metathesis reactions, though fast, all fall below the constraints of simple collision theory, and the reaction rate constants would be considered reasonable for small or zero activation energy reactions. Only for the reaction of $Cl + C_2H_6$ has the activation energy been measured, and it is very small, 170 ± 20 cal/mol.[32] It may be assumed that the much more exothermic reactions of $F + CH_4$ and $F + CH_3F$ have similar or even smaller activation energies.

Simple collision theory, historically, was put in the form of a collision frequency Z_c multiplied by a Boltzman factor to account for the activation energy and also a steric factor P_c to allow for the fact that not every collision had the requisite geometry for reaction:[33]

$$k = P_c Z_c \bar{e}^{E_c/RT} \tag{1}$$

Comparing this with the simple Arrhenius factors A and E, we see that

$$E = E_c + \frac{1}{2}RT$$

$$A = e^{1/2} P_c Z_c(T_m) \tag{2}$$

in which Z_c has a $T^{1/2}$ temperature dependence (when species are in concentration units), and we choose T_m as the mean reaction temperature at which studies have been made. $Z_c(T_m)$ is calculated at T_m.

Transition-state theory put all of this in a more detailed form, which allowed for structural changes in the reaction species in the transition state. In reactions with no measured activation energy a “contact transition state” has been defined corresponding to a suitably oriented collision at a collision diameter corresponding to a van der Waals contact.[34] Since there is no barrier to reaction, such a contact will always lead to products.

However there are detailed geometrical constraints on P_c which can be interpreted in terms of the fraction of orientations α_1 and α_2 of each of the two reacting species which can lead to reaction.[34,35] Finally there are electronic constraints, represented by $g_{el}^{\ddagger}$ (column 3, Table 3 and 4).

$$g_{el}^{\ddagger} = \frac{Q_{el}^{\ddagger}}{Q_{el}(1)\,Q_{el}(2)} \tag{3}$$

so that

$$k = g_{el}^{\ddagger}\alpha_1\alpha_2 Z_c e^{-E/RT} \tag{4}$$

$Q_{el}^{\ddagger}$ is the electronic partition function for the transition state while $Q_{el}(1)$ and $Q_{el}(2)$ are the electronic partition functions for reactants 1 and 2, respectively. For species in singlet electronic states having no electronic angular momentum and no low lying electronic states, $Q_{el} = 1$. For H atoms, $^2S_{1/2}$, $Q_{el}(H) = 2s + 1 = 2$, reflecting the electronic spin of 1/2. For halogen atoms F, Cl, Br, and I which have a ground state $^2P_{3/2}$, $Q_{el}(300\ K),(2j + 1) = 4$. F and Cl have low lying excited states $^2P_{1/2}$ which are only slightly above the ground state by about 1−2 kcal and give a small contribution to Q_{el} with increasing temperature.

All of the reactions listed in Table 4 correspond to recombinations of atoms with radicals, and the vibrationally excited state that is formed must be in its ground electronic state with no spin and no electronic angular momentum. Collisions that form triplet transition states or states with electronic angular momentum are on repulsive surfaces which do not lead to products. This is true even if the reaction path is not a complex one of addition followed by dissociation. Direct metathesis of $Cl + C_2H_5 \rightarrow HCl + C_2H_4$ would be constrained to go through a complex with no spin and no orbital angular momentum.

In similar fashion there are geometric constraints on recombinations. Thus the collision of Cl with $CH_3\dot{C}H_2$ must occur with the open Cl orbital overlapping the $C^{\bullet}$ orbital of the ethyl. A collision of Cl with the CH_3 or with the H atoms of the $\dot{C}H_2$ will not lead to recombination but instead to reflection. Thus the α_1 and α_2 represent the fractions of collision of species 1 and 2 with the proper geometric orientations for each species, respectively.

In Table 3 in which the reactions are atom + molecule, the transition states will all have the spin of the odd electron from the atom but will have no orbital angular momentum [these will all be ^2A (nonlinear) or $^2\Sigma$ (linear TS)]. Hence $Q_{el}^{\ddagger} = 2$.[49] For the first three reactions which are simple metathesis we have treated C_2H_6 as a cylinder, CH_3I as a slightly longer cylinder, and CH_4 as a sphere. The value used, $\alpha = 1$, for the molecule is an upper limit for a van der Waals collision. We notice that the observed rate constants for these species, though fast, yield rate constants smaller than the collision limit or even the collision limit with the electronic constraints.

For the last two reactions listed in Table 3, which represent atoms adding to double bonds, we have calculated from the reported rates a collision diameter subject to the electronic and geometrical constraints. The latter assume that only half of the collisions of Cl with C_2H_4 are active, collisions with the H atoms being reflective, and similarly for CH_2CO. Actually CH_2CO is more constrained since only collisions with the CH_2 end lead to the active intermediate $ClH_2C-\dot{C}=O$. On these grounds we might have expected $Cl + CH_2CO$ to have about half the rate of $Cl + C_2H_4$. Instead their rates differ by only 20%. The collision diameters for these last two reactions are 8 and 7 Å, respectively, and these are indeed too fast. There is no known reaction between small neutral species (excepting harpoon species) with this large a range of interaction. However these collision diameters are small compared to most of the values shown in Table 4.

An extreme example is given by the last reactions of $O +$ t-C_4H_9 with a collision diameter of 25 Å. The value calculated for the impact parameter from the modified Gorin model is 4.4 Å, almost 6-fold smaller. The reported rate constant is thus 32-fold larger than that calculated from the Gorin model.

The best known example in Table 4 is provided by the reaction of Cl with C_2H_5 to produce $HCl + C_2H_4$. It has a collision diameter of about 16 Å, reported in three different studies. One would normally say, "a well-studied reaction". In particular quite different techniques were used. However our own study[32] gives a value of 3.1 Å, about 5-fold smaller. The corresponding rate constant is 25-fold smaller. Thus there is a gross discrepancy between the two sets of studies. As a point of comparison, the value calculated from the modified Gorin model yields a value (Table 4) of $k_{298} = 2.7 \times 10^{-11}$ cm^3/(molecule s) about 2.3 times larger than our measured value but 10−13 times smaller than the other three values shown.

Conclusions

Detailed transition state analysis of atom abstraction with atoms, O_2, and radicals indicates that the kinetics of these reactions can lead to negative activation energies only in specific cases of multistep transition-state mechanisms which are in conformity with the six kinetic characteristics outlined in the introduction. Simple H atom abstraction reactions of the type $R^\bullet + HX \rightarrow RH + X^\bullet$ cannot take a multistep transition path since that will violate the equilibrium principle of transition-state theory and conflict with the demonstrated mechanism of the $RX + H \rightarrow R^\bullet + HX$ reaction. It is also evident that halogen atom abstraction from dihalides of the type $R^\bullet + X_2 \rightarrow RX + X^\bullet$ cannot follow a complex transition-state mechanism. Consequently, these abstraction reactions cannot have negative activation energies.

Some atom + molecule and especially atom + radical reactions show excessively large collision diameters. Some of their rates well exceed the van der Waals collision rate. However, no interaction is known between neutral species at such large distances.

The general features of the techniques used leading to negative activation energies for simple atom metatheses or too-fast rates are that they were all obtained from experimental systems using powerful laser flash initiation and the rates were measured on a millisecond time scale. Relaxation effects in these systems have not been explored extensively. They may be the source of some of the experimental artifacts. Some of our reservations concerning these flash techniques have been discussed in our earlier publications.[6,45]

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p 329, where the TS for the reaction of F + H_2, namely $[F{\cdot}H{\cdot}H]^{\ddagger}$, assumed linear, is labeled $^2\Pi$ with $Q_{el}^{\ddagger} = 4$ instead of $^2\Sigma$ with $Q_{el}^{\ddagger} = 2$. This lowers the *A*-factor by a factor of 2, making it a factor of 4 lower than the experimentally observed *A*-factor. This is poor agreement, which also suggests that the TS is bent rather than linear (see e.g.: Aoiz, F. J.; Banares, L.; Martinez-Haya, B.; Castillo, J. F.; Manolopoulos, D. E.; Stark, K.; Werner, H.-J. *J. Phys. Chem. A* **1997**, *101*, 6403, and Stark, K.; Werner, H.-J. *J. Chem. Phys*. **1996**, *104*, 6515, and references therein).

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