

# The Range of Chemical Forces and the Rates of Chemical Reactions<sup>†</sup>

SIDNEY W. BENSON

Loker Hydrocarbon Research Institute and Department of Chemistry, University of Southern California, University Park, Los Angeles, California 90089-1661

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## Introduction

Chemistry is the study of the changes in chemical substances. As such it involves the making and breaking of chemical bonds. Kinetics is the study of the rates at which these bond-making and bond-breaking processes occur. With the discoveries of the time-dependent Schroedinger equation and electron spin all the mysteries were removed from chemistry. But the additional step of providing useful answers to the rate behavior of many atom systems is still as elusive today as it was in 1926. To fill this otherwise forbidding vacuum, theoretical approaches have tended to be more or less empirical, using experimental data to guide the choice of approximations made or premises selected. In the present paper we shall outline an empiricism which has proven extremely useful in constructing a "theory" of chemical kinetics which today permits the quantitative estimation of rate constants for elementary chemical reactions.

Let us start by commenting on the first or perhaps zeroth law of chemistry which states that "...chemical substances cannot react until they are mixed." At the molecular level this translates into "...molecules can react only when they are in contact with each other." What do we mean by contact? There is no simple answer to this question. From a kinetic point of view we shall see that it will change with the nature of the reacting species and the particular elementary process under consideration. This is the case for the phenomenon which we wish to explore.

## The Potential Surface for a Molecular Process

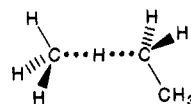
How do we construct a simple potential function for an elementary chemical reaction involving two species? Chemists have approached this problem by first considering the final products. Suppose we are interested in the reaction of a methyl radical with an ethane molecule. We need to know that these will undergo metathesis (the transfer of an atom between two particles, usually a radical and a molecule) and that the final products will be  $\text{CH}_4$  plus an ethyl radical. Such information comes only from experiments. There are no simple a priori methods for obtaining such information. The alternative, ab initio approach would be to consider all possible products of a  $\text{CH}_3 + \text{C}_2\text{H}_6$  collision and eliminate those which are thermochemically too endothermic for the energies (temperature) available.

Sidney W. Benson is Professor of Chemistry and Scientific Co-Director of the Hydrocarbon Research Institute at the University of Southern California. He was born in New York and received his A.B. degree from Columbia College. He received the Ph.D. degree from Harvard University in 1941, with G. B. Kistiakowsky. Dr. Benson was (1968-1983) Editor-in-Chief of the *International Journal of Chemical Kinetics*. He has been recognized as one of the major contributors in the field of chemical thermodynamics and kinetics.

Then one would have to solve the Schroedinger equation for all possible initial conditions, energies, and orientations interactions and eliminate all those for which the simple or complex path to products had to pass over too high an energy barrier. Finally for the remaining pathways one would have to deduce the one or more which had the lowest energy barriers and the highest probabilities. This ab initio approach seems hopeless in either the short- or long-range future. So let us continue with the empirical approach.

While it would seem that we are wedded to an infinite number of experimental inputs this is not really the case. It has been found that gas-phase reactions can be classified into a small number of categories involving the "molecularity" of the reaction and the nature of the chemical interaction.<sup>1</sup> As a consequence of this, the possible pathways are very limited.

In addition thermochemical data on reactants and products, generally available for most systems, allows us to restrict further the possible pathways to one or two probable reactions. We then make a verifiable assumption, namely that the reaction follows the "simplest" path from reactants to products. Thus in the example of  $\text{CH}_3 + \text{C}_2\text{H}_6$  metathesis we would assume that the carbon atom in the methyl radical bearing the odd electron must contact one of the H atoms in the ethane molecule. This gives rise to the TS Structure I.



Structure I

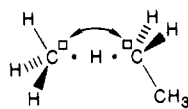
How do we deal quantitatively with such a structure and the collision or encounter which gave rise to it? Consider first the distances. The C...H distance between the methyl radical and the H atom must be shorter than the sum of their van der Waals radii since we know of no significant forces acting at longer range between the two particles. It must also be longer than the final bond length of 1.10 Å which they will have in the  $\text{CH}_4$  product. As we shall see this places this distance at between 2.9 and 1.1 Å. Similar considerations lead us to reach the same conclusions concerning the H...C distance in the ethane moiety of the TS.

We can further reduce the uncertainty in the distance by a knowledge of the activation energy barrier to the reaction. Experimentally it has been found that the

<sup>†</sup> This paper was presented in part at the Langmuir Award Symposium of the Spring Meeting of the American Chemical Society, New York, NY, April 1986.

(1) Benson, S. W. *Thermochemical Kinetics*, 2nd Ed.; Wiley: New York, 1976.

reaction has about an 11 kcal barrier. The reaction is also exothermic by about 6 kcal. From this data it is possible to conclude that this energy is used in forcing the C...H distance to be closer than van der Waals' contact. None of the other dispositions we might make of the activation energy such as bending deformations seem reasonable. Structure II is a valence-bond model of the TS



Structure II

with one-electron bonds between C and H and the third electron shared between the two C atoms and non-bonding with respect to the migrating H atom. Such a structure (which has an appealing symmetry with respect to reactants and products and seems energetically plausible since it has the same number of bonding electrons as both reactants and products) would then have C-H bonds much closer to normal C-H bonds. Using Pauling's rule for 1-electron bonds we assign them a distance about 0.3 Å longer or 1.4 Å. Compared to the van der Waals C...H-C distances of 2.9 + 1.1 = 4.0 Å we see that the half-bonded TS has a C·H·C distance of 2.8 Å, not very different. It has been customary to call these half-bonded transition states "tight".

If we wish to use the machinery of TST to calculate Arrhenius *A*-factors for the overall process we need to be able to assign moments of inertia and force constants to the TS structure. Using empirical relations we have chosen to divide the force constants for stretching and bending by factors of 2 leading to frequencies about 0.7 of the "normal" frequencies. Such an empirical approach has been extraordinarily successful in estimating, a priori, the Arrhenius *A*-factors for metathesis reactions.<sup>1</sup> Examining the methodology more closely we note that we have divided the reacting species into active and inactive zones in terms of their participation in the elementary reaction. The inactive zones have been assigned the geometries and properties essentially like those of the stable species while the active zones have had properties assigned on the basis of their closeness to the unperturbed species.

### Radical Recombination

The first successful attempt to use an empirical potential function to describe a chemical reaction was made by Gorin.<sup>2</sup> The large cross-sections which had been observed for the termolecular recombination of Br atoms suggested to him that the valence bond interaction between more complex radicals such as CH<sub>3</sub> might be significant at distances appreciably larger than the normal C-C bond length. Extending the Langevin model for ion-neutral interaction to neutrals he showed that there would be a critical distance, *r<sub>c</sub>* in the collision between two free radicals which would lead to their recombination. It is determined by the balance between centrifugal forces and valence forces. He employed a Lennard-Jones potential

$$V(r) = -\frac{2D_0r_0^6}{r^6} + \frac{A}{r^2} \quad (1)$$

(2) Gorin, E. *J. Chem. Phys.* 1939, 7, 263.

Here *D<sub>0</sub>* is the energy of the bond being formed whose ground state length is *r<sub>0</sub>*. The very short range (*r*<sup>-12</sup>) repulsive force was neglected at the large distances involved and the term  $A = P_\theta^2/2\mu$  where *P<sub>θ</sub>* is the constant angular momentum of the collision pair treated as two hypothetical mass points with a reduced mass *μ*, impact parameter *b*, and initial relative kinetic energy  $E_r^\circ = \frac{1}{2}\mu v_r^2$ . Then since  $P_\theta = \mu v_r b = \text{constant}$ :

$$A = E_r^\circ b^2 \quad (2)$$

When the methyl radical recombination was finally measured<sup>3a</sup> and shown to proceed at a rate equal to about 1/4 of all hard-sphere collisions *Z<sub>r</sub>*, only the Gorin model was close to the correct result.<sup>5b</sup> The critical distance *r<sub>c</sub>* turns out to be given by

$$(r_c/r_0) \sim (6D_0/RT)^{1/6} \quad (3)$$

with the rate constant (*ν* = mean molecular velocity):

$$k_r = g_{\text{elec}} Z_r = g_{\text{elec}} r_c^2 \nu \pi \quad (4)$$

*g<sub>elec</sub>* is the electronic partition function ratio. For larger radicals the Gorin model gave results too large compared to experiment by factors of up to 10. In an effort to rectify some of these discrepancies we proposed a restricted free-rotor model because even at the large distances predicted by the Gorin model, *r<sub>c</sub>/r<sub>0</sub>* ~ 2.5-3.0, radicals such as *tert*-butyl would in most orientations make van der Waals contact with their methyl groups.<sup>4</sup> This introduces a steric factor *α* into equation 4 with *α* varying between 1.0 and 0.01.

Unfortunately this restricted, free-rotor Gorin model still had difficulties with both small and large free radicals. A dynamical reworking of the Gorin model has recently led to some further constraints which now appear to give quantitative fits to the data on free radical recombination.<sup>5</sup> These constraints are as follows: (a) The volume occupied by the unpaired electron is restricted by the volume occupied by its neighboring bonded electrons. For a flat CH<sub>3</sub> radical this means that only 55% of the space around the central C atom contains the odd electron. (b) It is assumed that for exchange forces (valence forces) to operate, the collision pair at the critical impact parameter must have an orientation such that the odd-electron space on each radical center is in contact with its counterpart.

These constraints lead to a relatively simple model in which we draw a sphere around each radical center equal to 1/2 (for symmetrical radicals) the Gorin critical impact parameter *b<sub>c</sub>*. We then project the van der Waals radius of each bonded atom on the surface of this sphere. The latter areas are then inactive while the remaining areas are "active" (Figure 1). The steric factor *α* (Table I) is then ≥ the product of fractions of active area *β<sub>i</sub>* on each sphere. In cases such as *tert*-butyl, allyl, etc. where bonded groups project beyond the Gorin sphere not all contacts between active areas are possible and a further steric correction must be made. Table I shows the comparison of predicted and observed values for the recombination rate constant *k<sub>r</sub>*. The agreement is well within the experimental uncertainty in all cases for the first time.

(3) (a) Gomer, R.; Kistiakowsky, G. B. *J. Chem. Phys.* 1951, 19, 85. (b) Benson, S. W. *Adv. Photochem.* 1964, 2, 1.

(4) Reference 1, Sections 3.6 and 4.8.

(5) Benson, S. W. *Can. J. Chem.* 1983, 61, 881.

Table I.  
Data on Recombination Rate Constants for Free Radicals: Restricted Free-Rotor Model with Correction for Electron Exchange

radicals	$\log k_r(\text{exptl}),$ L/(mol-s) <sup>a</sup>	$r^*, \text{ \AA}$ calcd	$\log g_c Z_r,$ L/(mol-s) <sup>b</sup>	$\alpha,^c$ exptl	$\beta_i \beta_j,$ calcd	$\beta_i,$ calcd
2CH <sub>3</sub>	10.4	5.37	10.79	0.39	0.30	0.55
2C <sub>2</sub> H <sub>5</sub>	10.0	5.29	10.63	0.25	0.18	0.42
2 <i>i</i> -C <sub>3</sub> H <sub>7</sub>	9.7	5.24	10.53	0.15	0.10	0.31
2 <i>t</i> -Bu	9.1	5.19	10.48	0.043	0.029	0.17
Me - <i>t</i> -Bu <sup>d</sup>	10.2 ± 0.3	5.30	11.05	0.12	0.10	0.55/0.19
2 Allyl	9.9	4.72	10.75	0.12	0.16	0.41
2CF <sub>3</sub>	9.7	5.44	10.55	0.15	0.14	0.38
2CCl <sub>3</sub>	9.6	5.34	10.30	0.12	0.07	0.27
Cl + CCl <sub>3</sub>	9.8	6.02	10.65	0.23	0.27	0.27

<sup>a</sup> Experimental values from ref 3. <sup>b</sup> Calculated using  $r^*$  (calcd) and  $g_c = 1/4$ .  $Z_r = \pi(r^*)^2 v / \sigma$  where  $v$  = relative velocity at 300 K and  $\sigma = 2$  for identical radicals. <sup>c</sup> From experimental data and eq 4. <sup>d</sup> Using dissociation rate constant of ref 10, of a bond dissociation energy of 83.5 kcal/mol, and an estimated  $\Delta S^\circ(300) = 45 \pm 1.5$  eu to calculate  $k_r$  at 800 K.

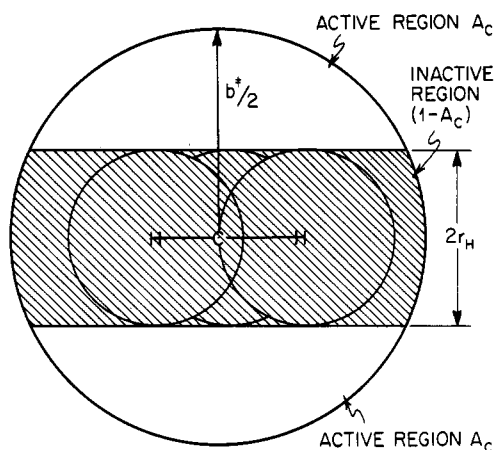


Figure 1. Methyl radical in projection showing regions active and inactive (shaded) in recombination  $r_H$  is the van der Waals radius of the H atom;  $b^*$  is the impact parameter for recombination. The third H atom is behind the two shown.

### Simple Bond Fission

The inverse reaction to radical recombination is simple bond fission. We divide the category of fission reactions into two classes, simple and complex. By simple bond fission we mean the breaking of one bond in a molecule leading to two free radicals. Complex fission may involve the breaking of two or more bonds, with possible making of other bonds. The cleavage of ethane into two methyl radicals is a simple bond fission. The transition states must be the same for simple bond fission and radical recombination. Their rate constants are related to each other thermodynamically by the equilibrium constant  $K_f$  for bond fission:

$$K_f = k_f/k_r \quad (5)$$

It is this thermodynamic relation which has provided much of the continued interest in the TS for simple bond fission. Historically one of the primary methods for the measurement of the heats of formation of radicals has come from measurements of the rate constant  $k_f$ . Since radical recombination appears to have little or no activation energy,  $E_f$  the activation energy for  $k_f$  could be equated with the bond dissociation energy. (We must distinguish here between bond dissociation enthalpy  $DH^\circ$  and bond dissociation energy  $DE^\circ$ .  $DH^\circ = DE^\circ + RT$  for ideal gases.) If  $k_r$  were known and the entropies of the radicals were known, then a single measurement of  $k_f$  at a single temperature would provide a better measure of  $E_f$  than that obtained from an

experimental Arrhenius plot. A lively controversy is still current<sup>6-9</sup> because of the discrepancy of the order of about 2 kcal which appears to exist between this method of obtaining  $\Delta H_f^\circ$  of the alkyl radicals and that obtained from iodination techniques.<sup>8</sup>

In any case we see that if the modified Gorin model for recombination is correct, then we can calculate the rate constant  $k_f$  from a knowledge of  $k_r$  and  $K_f$ .  $K_f$  can be calculated if the entropies and enthalpies of the appropriate radicals and the parent molecule are available. If some of this data is lacking, then at a minimum we can calculate the Arrhenius A-factor,  $A_f$ , since  $A_f$  and  $k_r$  are related:<sup>1</sup>

$$\ln \left[ \frac{A_f}{k_r} \right] = \frac{\Delta S_f^\circ}{R} \quad (6)$$

Note that since  $\Delta S_f^\circ$  (the standard entropy change in the bond fission) is a function of temperature then  $A_f$  may be also expected to vary with temperature. The temperature dependence of the unimolecular rate constant for bond fission is of great interest. Transition-state theory (TST) which provides the general foundation for most modern kinetics represents the rate constant as

$$k = \frac{(k_B T)}{h} e^{\Delta S^\ddagger/R - \Delta H^\ddagger/RT} \quad (7)$$

where  $k_B$  is the Boltzman constant and  $h$  is Planck's constant. The relation to the Arrhenius form of the rate constant,  $Ae^{-E/RT}$  is given by

$$A = \frac{(ek_B T_m)}{h} e^{\Delta S_m^\ddagger/R} \quad E = \Delta H_m^\ddagger + RT_m \quad (8)$$

where  $T_m$  is the mean experimental temperature and  $\Delta S_m^\ddagger$  is the entropy change in going from reactant to the transition state at  $T_m$ . For the Gorin model of nearly free particles weakly interacting at a distance close to 3 times the initial bond distance, there is a large increase in entropy and in consequence  $A$  is much larger than  $10^{13} \text{ s}^{-1}$ , generally in the range  $10^{16 \pm 1} \text{ s}^{-1}$ . This has given rise to its description as a "loose" transition state. In going to this transition state, 6 internal degrees of freedom consisting of a bond stretch, 4 rocking modes,

(6) Tsang, W. *J. Am. Chem. Soc.* 1985, 107, 2872. Tsang, W. *Int. J. Chem. Kinet.* 1978, 10, 821.

(7) McMillen, D. F.; Golden, D. M. *Annu. Rev. Phys. Chem.* 1982, 33, 493.

(8) Pacey, P. D.; Wimalasena, J. H. *J. Phys. Chem.* 1984, 88, 5657.

(9) Choo, K. Y.; Beadle, P. C.; Piskiewicz, L. W.; Golden, D. M. *Int. J. Chem. Kinet.* 1976, 8, 45.

and an internal rotation are transformed into 3 translational and 3 rotational degrees of freedom. One of the translational modes is the reaction coordinate which gives rise to the term  $k_B T/h$ . If the reactant modes are high frequency, then  $\Delta C_v^*$  can be as much as  $7/2R$  at low temperature and  $-5/2R$  at very high temperature. At intermediate temperatures  $\Delta C_v^*$  could be close to zero.

The uncorrected Gorin model yields a value of  $k_r$  which increases with temperature as  $T^{1/6}$  when steric factors are close to unity as they are for  $\text{CH}_3$ . For bulky radicals however, since  $r_c$  varies as  $T^{-1/6}$ , the Gorin spheres grow smaller with increasing temperature and nonbonded interactions can make the nonallowed contacts disproportionately larger. There is no simple explicit way of representing this, but it can lead to a decrease in recombination rate of *tert*-butyl radicals of about a factor of 5 between 300 K and 900 K.<sup>9</sup> Since the Gorin radius varies as  $T^{-1/6}$ , the projected van der Waals area  $A_v$  which is a constant, becomes a larger fraction of the radical surface which varies as  $T^{-1/3}$ . Thus  $\beta_i$  the "active" area of the radical which appears in  $k_r$  as a product (one for each radical) may be expected to decrease nonlinearly with increasing temperature.  $\beta_i$ , aside from nonbonded steric interactions varies as

$$\beta_i = 4\pi \left( \frac{b_c^2}{2} \right) - A_v = \pi b_{cm}^2 \left( \frac{T_m}{T} \right)^{1/3} - A_v \quad (9)$$

where  $b_{cm}$  is the critical impact parameter at  $T_m$ . With the exception of *tert*-butyl radicals, the data on radical recombination is not accurate enough to explore the validity of eq 9.

### Radical Disproportionation—Metathesis

The transfer of an atom between two particles in metathesis has a small intrinsic activation energy in the range  $8 \pm 3$  kcal/mol. For very electronegative atoms or radicals it can be close to zero.<sup>10</sup> The disproportionation of two free radicals is a metathetical reaction with quite generally a zero activation energy. This finding appears to be quite unrelated to the electronegativity of the radicals. It is a special case of the metathesis class in that it also appears to have an Arrhenius  $A$ -factor about 20-fold larger than that found for the typical radical-molecule metathesis. If we are to describe it in terms of range, it has a range of about 4.0 Å for alkyl radicals, intermediate between the tight transition state characterizing the typical metathesis and the loose transition state of recombination. There is no obvious long or intermediate range force acting in disproportionation, and it has taken some time to find a suitable model to describe it. This has recently been done successfully in terms of what has been labeled, the "contact" transition state.<sup>11</sup>

The contact-transition-state geometry is determined by the requirement that the atom bearing the odd electron and the atom being transferred be in van der Waal's contact with each other. In the case of two ethyl radicals, for example, the  $\text{C}^* \cdots \text{H}$  distance would be 2.9 Å corresponding to a 1.7-Å radius for  $\text{C}^*$  and a 1.2 Å radius for H. Since the H is attached to a  $\beta$ -carbon atom with a C-H bond length of about 1.10 Å, the linear

Table II.  
Rate Constants for Radical Disproportionation:<sup>a</sup>  
Comparison of Observed and Calculated Values

R. + H donor	$\mu_r$	$10^{-9} g_e Z_c n_{Me}$	$\beta_R$	$\beta_H$	$10^{-9} k_d$	
					est	obsd
Me + Et	10.0	32	0.26	0.32	1.9	1.4
Et + Et	14.5	27	0.26	0.22	1.5	1.4
<i>i</i> -Pr + <i>i</i> -Pr	21.5	77	0.26	0.21	2.4	2.5
<i>t</i> -Bu + <i>t</i> -Bu	28.5	58	0.26	0.20	3.0	3.2

<sup>a</sup> All  $k_d$  and  $Z_c$  in L/(mol·s);  $\mu_r$  in amu.  $n_{Me}$  is the number of Me in the H donor: 1 for Et, 2 for *i*-Pr, and 3 for *t*-Bu. Restriction of 45° twist on incipient  $\pi$ -bond.  $\beta_H = 3\theta_{1H} \times 1/2$  for orientation of  $\pi$ -bond. Use  $\theta \leq 39^\circ$  for  $\text{C}^\circ$  ( $\beta_R$ ).

$\text{>C}^* \cdots \text{H-C} \leftarrow$  distance is 4.0 Å. In the chemical reaction the H atom would move 1.8 Å to form the new C-H bond.

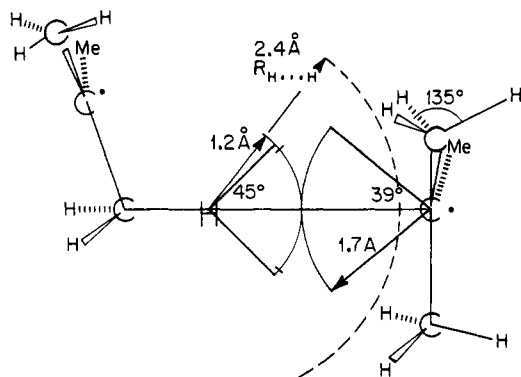
As in the case of the loose recombination model, it is easier to describe the loose disproportionation transition state in terms of accessible contacts and geometry. These are (1) If we draw van der Waals spheres around the radical center and the metathesizing atom, then we have two angles about the  $\text{>C}^* \cdots \text{H}$  bond and two more about the  $\text{H-C} \leftarrow$  bond which can vary with no change in potential subject only to the constraint that all other atoms in the two systems be no closer than van der Waals radii permit. (2) For a linear  $\text{>C}^* \cdots \text{H-C} \leftarrow$  geometry an internal rotation is free subject to the same van der Waals constraints. For a nonlinear geometry two internal rotations have these constraints. (In the linear geometry we have 2 degenerate  $\overline{\text{C}} \cdots \text{H} \cdots \overline{\text{C}}$  bending motives at right angles to each other. One of these changes to an internal rotation in the nonlinear geometry.) (3) The odd electron whose van der Waals radius from C is taken as 1.7 Å is confined to  $\leq 45^\circ$  azimuth angle about the symmetry axis of the  $\text{>C}^* \cdots$  radical. (4) Since the driving force for the very exothermic disproportionation is double-bond formation in the radical losing the H atom from its  $\beta$ -position, the groups attached to it must lie in or near a dihedral plane within  $45^\circ$  of the emerging double bond. This essentially restricts the effective configurations by a factor of  $1/2$ .

The assumption of essentially square-well type potentials restricting the angular deformations require the equivalent of a five-dimensional integration. In the actual computations done thus far<sup>11</sup> these have been done only crudely with considerable simplification, the estimated uncertainty being of the order of 20%. Despite this, as can be seen from Table II, the agreement between observed and estimated values is well within the experimental uncertainties. Figure 2 shows a van der Waals contact between two *tert*-butyl radicals in disproportionation.

In this model for disproportionation we have ignored any forces acting between the radical  $\text{C}^*$  and the H-C bond. If there are weak van der Waals forces or even weak dipole-dipole forces<sup>5</sup> at the distances involved, we might expect a temperature dependence for disproportionation very similar to that for recombination, that is a slowly decreasing rate with increasing temperature or perhaps a temperature independence. For example, methoxy radicals,  $\text{CH}_3\text{O}$ , have an extremely rapid rate of disproportionation and an estimated dipole moment of about 1.0 D. One would expect that at distances of the order of 3.5 to 4.0 Å there would be significant

(10) Alfassi, Z. B.; Benson, S. W. *Int. J. Chem. Kinet.* 1973, 5, 879.

(11) Benson, S. W. *J. Phys. Chem.* 1985, 89, 4366.



**Figure 2.** van der Waals contact in 180° geometry for the disproportionation of two *tert*-butyl radicals. Arcs show permitted contact between C...H.

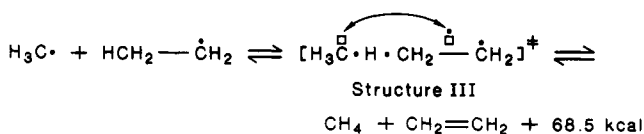
(compared to  $RT$ ) forces operating to produce head-to-tail collisions between two  $\text{CH}_3\text{O}$  radicals. Disproportionation of  $\text{CH}_3\text{O}$  should then show a small negative activation energy. No data is available for comparison.

### Radical-Molecular Metathesis

These reactions have low intrinsic activation energies in the range of 0 to 15 kcal/mol. As we observed earlier in our discussion of the  $\text{CH}_3 + \text{C}_2\text{H}_6$  reaction, it is felt that this intrinsic activation energy is localized in the relative translational energy of the reacting pair and is required to provide energy for the radical center to penetrate the electron shell of the atom being transferred.

The intrinsic activation energies for these reactions are quantitatively correlated with the electron affinities of both the entering and leaving radicals.<sup>10</sup> Halogen atoms with the largest electron affinities have the lowest intrinsic activation energies. Alkyl radicals with the lowest electron affinities have the highest  $E_{\text{act}}$ . One may ask two questions. Why do radical-radical metatheses have both zero  $E_{\text{act}}$  and much larger  $A$ -factors?

In the absence of a rigorous knowledge of the potential energy surface, we can only suggest a plausible response to the first question. In valence-bond terms, the typical metathesis reaction can be described as a 3-center, 3-electron system. The two  $\sigma$ -bonding electrons of the atom being transferred are still  $\sigma$ -bonding in the transition state while the odd radical electron is shared between the entering and leaving radicals. It is nonbonding with respect to the transferring atom and is thus excluded from the region of this atom in the transition state. One might suggest that the intrinsic activation energy for the metathesis is the price paid to localize the odd electron on either radical. (In Structures such as II or III there is a formal change of  $+1/2$  at each carbon atom with the odd electron divided between them.) When either radical has an appreciable electron affinity, the energy is accordingly lowered. When either group, leaving or entering is itself a free radical with open orbitals, then the odd electron can be converted into a bonding electron (Structure III).



The odd electron becomes part of the emerging  $\pi$ -bond in the olefin product. This is consistent with the

observation that  $\text{CH}_3\text{O}$  disproportionation is weakly chemiluminescent with production of an excited state of  $\text{CH}_2\text{O}$ . This was for a long time a somewhat paradoxical effect since the usual rule in exothermic metathetical reactions is that the exothermicity went into the newly formed bond. In the case of radical disproportionation, the exothermicity of the reaction arises from  $\pi$ -bond formation in the emerging olefin. Thus in fact the rule is obeyed.

If the foregoing is a plausible description of the zero activation energy for radical disproportionation, then the relatively high  $A$ -factor for these metatheses is also a consequence of the fact that we have an "early" transition state, namely, as soon as van der Waals contact is established, there is no further barrier to reaction.

With the rules described earlier for tight TS states it is possible to estimate Arrhenius  $A$ -factors to within a factor of 2. This amounts to estimating  $\Delta S^\ddagger$  to within 1.4 eu. Experimental determination of  $A$ -factors are seldom reliable to better than a factor of about 3 to 4.

Over any extended temperature range it is now well known that the two-parameter Arrhenius equation is inadequate and that the three-parameter equation

$$k = AT^m e^{-E/RT} \quad (10)$$

must be used in its place. One of the triumphs of TS Theory has been its success in providing reliable estimates of the exponent<sup>1,12,13</sup>  $n$  which can be related to a heat capacity of activation:

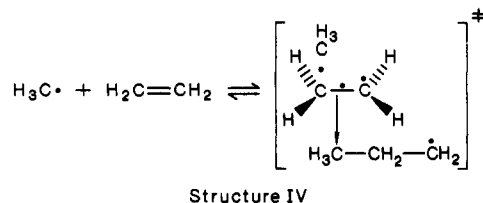
$$n = \Delta C_v^\ddagger / R \quad (11)$$

For many radical-molecule reactions, particularly those of importance in flames the effective values of  $n$  between 300 and 1500 K is in the range 2 to 2.5. Arrhenius plots will show considerable curvature and linear extrapolations from either low or high temperatures can be in error by factors as large as 100.

With the above mentioned empirical rules and TS Theory one can estimate from the measurement of the rate constant at a single temperature, all three parameters in the modified Arrhenius eq 10.

### Radical Addition to Multiple Bonds

The valence-bond description of radical-molecule metathesis suggests that it is the  $\sigma$ -bond electrons that are truly the active actors in the reaction. For this reason we have suggested that atom metathesis is best and more generally described as  $\sigma$ -bond metathesis. This description becomes more apparent when we look at the addition of atoms or free radicals to multiple bonds, on the face of it a totally different type of reaction. For  $\text{CH}_3$  addition to  $\text{C}_2\text{H}_4$ , the transition state would be Structure IV.



(12) Cohen, N. *Int. J. Chem. Kinet.* 1982, 14, 1339; 1983, 15, 503 (erratum).

(13) Cohen, N.; Benson, S. W. *J. Phys. Chem.*, in press.

Again we are dealing with a 3-center, 3-electron process. In  $\sigma$ -bond metathesis we convert a  $\sigma$ -bond into a new  $\sigma$ -bond. In what we have labeled  $\pi$ -bond metathesis, the addition of radicals to multiple bonds, we convert a  $\pi$ -bond into a  $\sigma$ -bond. The final product in addition is a single-radical species while in metathesis it is a pair of species, one of them a radical.

The electronic description of the addition reaction suggests that it should resemble metathesis and that in fact is exactly what is observed.<sup>1</sup> Intrinsic activation energies are low, in the range 0 to 12 kcal/mol. They tend to decrease with increasing electron affinity of the attacking radical and with decreasing ionization potential of the olefin and have been historically described as "electrophilic reactions". This has been sometimes more apparent than real. Szwarc<sup>14</sup> showed some 30 years ago that the methyl affinity of aromatic molecules was strongly correlated with their localization energies (LE). (This is a measure of the  $\Delta H_f^\circ$  of the resulting free radical.)

Parallel to the observation for sigma bond metathesis that as  $E_{act}$  approaches 0, the TS changes from tight to loose (or to a contact TS) we find in  $\pi$ -bond metathesis the same trend. As  $E_{act} \rightarrow 0$ , the  $A$ -factor increases significantly and we go from a tight TS to a contact TS. In the case of Cl or Br atom addition to  $C_2H_4$ , the activation energies are close to zero and the  $A$ -factors are very high. Bayes<sup>16</sup> has shown that the rate constants for radical additions to  $O_2$  and  $O_3$ , for all of which  $E_{act} = 0$ , the  $A$ -factors are logarithmically correlated with the difference between ionization potential (radical) and electron affinity (substrate).

### Complex-Potential-Surfaces-Cage Effects in Gases

The typical chemical reaction has been so far treated as though it involved the passage of a critically activated species over a potential-energy maximum. What if the potential energy surface is more complex, if it involves more than one maximum or a long range interaction? Under these circumstances the kinetic behavior can show unexpected features. Let us consider some examples from the category of bimolecular reactions.

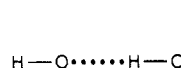
Radical recombination appears to be dominated by valence forces which have a typical range of about 4 to 6 Å depending on the strength of the bond and its length. Disproportionation of alkyl radicals on the other hand, with the contact transition state appears to have no significant potential associated with it. The modified Gorin model, however, has significant angle dependence associated with the valence potential so that in a collision between two radicals where both paths are available, the branching ratio is dominated by the relative orientation at distances in the 4–6-Å range. Suppose now that we are dealing with polar radicals with dipole moments of from 1 to 2 D. These may have interactions of the order of 0.5 to 1.0 kcal in the same range 4 to 6 Å with strong angle dependence. What influence will this have on the reaction? Depending on the relative strength and angle dependence of the two potentials they may enhance or reduce either of the alternate reaction pathways.

(14) Levy, M.; Szwarc, M. *J. Am. Chem. Soc.* **1955**, *77*, 1949.

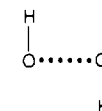
(15) Fueno, T.; Benson, S. W. *J. Chem. Phys.* **1962**, *36*, 1597.

(16) Paltenghi, R.; Ogryzlo, E. A.; Bayes, K. D. *J. Phys. Chem.* **1984**, *88*, 2595.

Hydroxyl radicals (OH) have a dipole moment of 1.5 D. In the head-to-tail orientation (Structure V) they

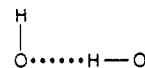


Structure V



Structure VI

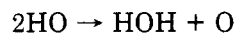
would have an attraction interaction of 0.5 kcal at a separation of 5 Å. (The very rapid OH rotation produces a rapidly oscillating dipole field which contribute very complex dynamical effects to such an interaction. Large differences in rotational quantum numbers of two approaching OH radicals would work to prevent significant dipole interaction.) The Gorin model yields a valence bond interaction of 0.5 kcal at about 4.0 Å. Its orientation dependence favors an O...O approach at right angles to the two OH planes of rotation. In such an approach the dipole interaction is minimized (Structure VI). In this case it would appear that the potentials do not influence the relative branching. However Structure V does not have the proper bond angles for  $H_2O$  formation. The optimum structure for disproportionation is shown in Structure VII for which the dipole interaction is negligible.



Structure VII

Since however Structures V and VII differ by less than a 90° orientation of one OH, one may well ask if the two radicals might not approach along a head-to-tail path V and then rotate over to the H-bonded structure of VII before separating? If in fact hydrogen bond formation involves a deformation of the symmetrical  $\pi$  orbital on oxygen, then the actual potential may actually favor such a rotation at small separations. In this case the dipole attraction acts as a long-range potential trap for the disproportionation.

Experimental data on the reaction<sup>17</sup> yield at 300 K either zero or a very small activation energy (1 kcal) for the reaction



with a larger activation energy at flame temperatures of about 3–5 kcal. The rate constant at 300 K is about  $10^{9.2}$  L/(mol s) which would correspond to a contact transition state with very little solid angle available for the O...H-O doubly degenerate bend in Structure VII. This assumes an O...H-O distance of about 2.8 Å similar to the O...HO separation in ice.

While it is not common to describe such interactions in these terms, it is quite reasonable to talk of an "attractive cage" in the OH interaction and one may indeed expect to see such cage effects in other systems. One which has evoked much interest recently has been the simple fission of  $\text{CH}_3\text{NO}_2$ . Dewar had observed<sup>18</sup> that many pyrolysis studies had been reported in which the activation energy observed was significantly less than the bond dissociation energy of some 60 kcal. He proposed on the basis of some MINDO calculations that

(17) *CRC Handbook of Bimolecular and Termolecular Gas Reactions*; Kerr, J. A., Moss, S. J. Ed.; CRC Press Inc.: Boca Raton, FL, 1981, Vol. II Table 203.

(18) Dewar, M. J. S.; Ritchie, J. P.; Alster, J. *J. Org. Chem.* **1985**, *50*, 1031.

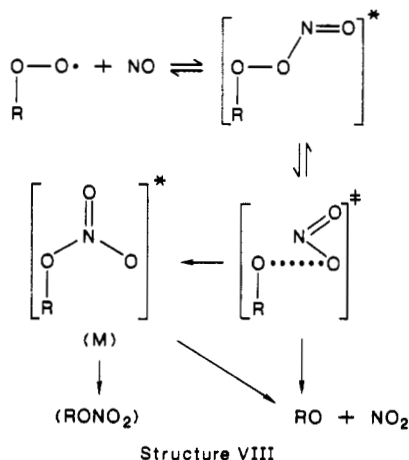


it should be possible for  $\text{CH}_3\text{NO}_2$  to isomerize to  $\text{CH}_3\text{ONO}$  at an energy of about 55 kcal. While the isomerization is nearly thermoneutral,  $\text{CH}_3\text{ONO}$  has a relatively weak 40 kcal bond between  $\text{CH}_3\text{O}$  and  $\text{NO}$ . In consequence the overall decomposition would produce quite different from expected radicals at a much faster rate.

In support of such a cage effect is the observation by Lee et al.<sup>19</sup> of the formation of  $\text{NO}$  in a time-of-flight, beam, IR multiphoton dissociation of  $\text{CH}_3\text{NO}_2$ . They estimate an activation energy of about 56 kcal for the process leading to  $\text{NO}$ . Further support comes the observation of Golden et al.<sup>20</sup> that under collision-free conditions excited nitrobenzenes can eliminate  $\text{NO}$  and form phenoxy radicals in competition with phenyl +  $\text{NO}_2$  formation.

Such observations imply interesting consequences for the recombination of  $\text{CH}_3 + \text{NO}_2$  which has been reported to go to both  $\text{CH}_3\text{NO}_2$  and  $\text{CH}_3\text{ONO}$  at ratios in the range 1:1 to 2:1 respectively. The path leading to  $\text{CH}_3\text{NO}_2$  forms an energized species capable of isomerizing to  $\text{CH}_3\text{ONO}$ . Hence as the pressure is lowered we should see increasing amounts of  $\text{CH}_3\text{ONO}^*$  formed at the expense of  $\text{CH}_3\text{NO}_2^*$ . At the pressures where this is observed we should in fact see only  $\text{CH}_3\text{O} + \text{NO}$  products since the fission of  $\text{CH}_3\text{ONO}^*$  will be very much faster than the isomerization of  $\text{CH}_3\text{NO}_2^*$ .

In related work, Atkinson et al.<sup>21</sup> have reported that in the very important atmospheric reaction of  $\text{RO}_2$  radicals with  $\text{NO}$ , significant quantities of  $\text{RONO}_2$  are formed in competition with the expected products  $\text{RO} + \text{NO}_2$ . The proportion of alkyl nitrate produced increases at higher pressures and with increasing size of  $\text{R}$ , reaching 50% at  $\text{R} = \text{hexyl}$ . This is the behavior to be expected if the nascent  $\text{ROONO}^*$  with about 35 kcal of internally released bond energy breaks with weak 20 kcal  $\text{O}-\text{O}$  bond. If the critical  $\text{O}\cdots\text{O}$  bond distance at rupture is about 4.0 Å, then a small rotation of the departing  $\text{NO}_2$  group can bring the  $\text{O}$  atom of  $\text{RO}$  and the  $\text{N}$  atom of  $\text{NO}_2$  into range and proper angular orientation to form the much stronger 40 kcal  $\text{RONO}_2$  bond as illustrated in Structure VIII.



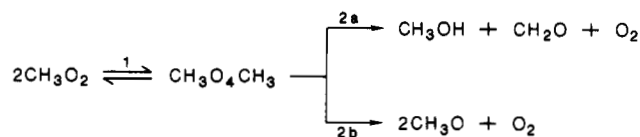
These potential cages suggest a resolution to one of the most puzzling reactions in combustion, the self-

(19) Wodtke, A. M.; Hints, E. J.; Lee, Y. T. *J. Chem. Phys.* 1986, 84, 1044.

(20) Gonzales, A. C.; Larsen, C. W.; McMullen, D. F.; Golden, D. M. *J. Phys. Chem.* 1985, 89, 4809.

(21) Atkinson, R.; Aschman, S. M.; Carter, W. P. L.; Winer, A. M.; Pitts, J. N., Jr. *J. Phys. Chem.* 1982, 86, 4563.

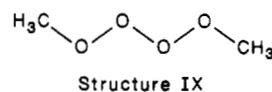
termination of alkyl peroxy radicals ( $\text{RO}_2$ ). It has recently been demonstrated that in the gas phase, two  $\text{CH}_3\text{O}_2$  radicals react in two competing pathways at rates of the order of  $10^{8.3} \text{ L}/(\text{mol}\cdot\text{s})$ .<sup>22</sup>



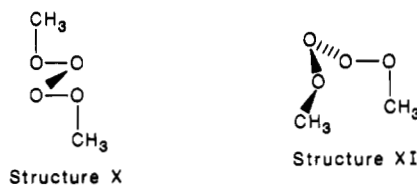
Reaction 1 is expected to be in equilibrium except at very low pressures and is about 9 kcal exothermic. The branching ratio  $k_{2a}/k_{2b}$  has been reported in the range 2.0 to 1.0.<sup>24</sup> No extended temperature dependence has been reported for  $k_2$  or the branching ratio.

About 30 years ago Russell<sup>25</sup> proposed that for solution reactions the termination takes place via a typical ENE type mechanism in analogy with similar reactions observed with unsaturated systems. This mechanism involves an internal 1, 5 H atom shift and in the usual system has an intrinsic activation energy of about 30–35 kcal. It is clearly not to be expected in the saturated tetraoxide where even higher activation energies would be anticipated. In the latter the very rapid reaction observed for  $2\text{CH}_3\text{O}_2$  would require for the tight transition state involved, an intrinsic activation energy measured from the ground state of the  $\text{R}_2\text{O}_4$  of not more than 4–6 kcal,<sup>26</sup> giving a overall negative activation energy of from 5–3 kcal for the path 2a.

In solution oxidations, the results are obscured by the very rapid disproportionation which has been independently observed for  $\text{CH}_3\text{O}$  radicals. If for example only path 2b were operative, the  $\text{CH}_3\text{O}$  radicals would be formed in a solvent cage with overwhelming probability of disproportionating before escape by diffusion. It now seems likely that in the gas phase the production of two alkoxy radicals via path 2b could account for the path 2a products if the alkoxy radicals for example have a dipole moment of about 1.0 to 1.2 D. At 4.0-Å separation they could have an attraction of about 0.5 kcal in a head-to-tail orientation. Even in the all-trans conformation (Structure IX) the mean separation of the



$\text{CH}_3\text{O}$  groups is about 5 Å while in any of the gauche conformations (X,XI) they come within 4 Å. The



proposed Russell transition state, involving a 1, 5 H shift from  $\text{CH}_3$  to the  $\text{OCH}_3$  would bring them to less than 3 Å apart. It thus seems reasonable to suggest that for  $\text{RO}_2$  termination where disproportionation can occur, the only path operative is the concerted path 2b

(22) Parkes, D. A.; Paul, D. M.; Quinn, C. P.; Robson, R. C. *Chem. Phys. Lett.* 1973, 23, 425.

(23) Adachi, H.; Basco, N. *Int. J. Chem. Kinet.* 1982, 14, 1125, 1243.

(24) L. Batt *Int. Rev. Phys. Chem.* 1986, 2, 1.

(25) Russell, G. A. *J. Am. Chem. Soc.* 1957, 79, 3871.

(26) Benson, S. W. "The Mechanism of Pyrolysis, Oxidation and Burning of Organic Materials"; *NBS Spec. Publ. (U.S.)* 1972, No. 357; p 121.

producing alkoxy radicals. Where their orientation and kinetic energy is such that they can be contained by their dipole attraction, then disproportionation occurs to the path 2a products. The monotonically decreasing rate constant  $k_t$  observed in the sequence  $\text{MeO}_2$ ,  $\text{EtO}_2$ ,  $i\text{PrO}_2$ ,  $t\text{BuO}_2$ <sup>24</sup> could then be accounted for by an activation energy changing from 2 kcal for  $\text{MeO}_2$  to the observed 9 kcal for  $t\text{-BuO}_2$ . Measured from the tetraoxide ( $\text{R}_2\text{O}_4$ ) these activation energies would range from 11 to 18 kcal. \*H/D isotopic effects which have been reported have recently been shown by Mendenhall and Quinga to also occur in hyponitrite decompositions where only the 2b path is available.<sup>27</sup>

A last word on the subject of cage effects in gas reactions. In mass spectrometry we frequently find quite extensive rearrangements. In the fission of an excited cation  $\text{AB}^+$  (produced by the electron bombardment of

(27) Mendenhall, G. D.; Quinga, E. M. Y. *Int. J. Chem. Kinet.* 1985, 17, 1187.

AB) to produce  $\text{A}^+ + \text{B}$  fragments, we will expect a relatively long range attraction arising from ion-dipole or ion-induced dipole forces. Either of these can extend out to 6 to 9 Å and result in an extended cage effect leading to multiple encounters between  $\text{A}^+$  and B. Such secondary encounters could produce some of the rearrangements observed without requiring very complex and tight transition states.<sup>28,29</sup>

*I wish to express my appreciation to the American Chemical Society for the honor of being chosen as the Langmuir medalist for 1986 and for the opportunity to present this work on the occasion. Many of the results presented arise from the contributions over the past 25 years of students, postdoctorates, and colleagues too numerous to mention. In the past decade funding for much of this work has come from grants provided by the National Science Foundation and the U.S. Army Research Office.*

(28) Dodd, J. A.; Golden, D. M.; Brauman, J. I. *J. Chem. Phys.* 1984, 80, 1894; 1985, 82, 2169.

(29) de Puy, C. H. In "Ionic Processes in the Gas Phase", Ferreira, M. A. A., Ed. Reidel: Dordrecht, The Netherlands, 1984, pp 227-241.

## High-Oxidation-State Molybdenum and Tungsten Alkylidyne Complexes

RICHARD R. SCHROCK

Department of Chemistry, 6-331, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139

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Carbon forms triple bonds to few elements besides itself, nitrogen, and oxygen. The first triple bonds between a transition metal and a monosubstituted carbon atom were found by Fischer in chromium, molybdenum, and tungsten complexes of the type  $\text{M}(\text{CR})(\text{CO})_4(\text{halide})$ .<sup>1</sup> Molybdenum and tungsten complexes of the type  $\text{M}(\text{C}-t\text{-Bu})(\text{CH}_2-t\text{-Bu})_3$  that were discovered several years later<sup>2</sup> at first appeared to be only a rather limited class of distant cousins of the Fischer complexes, but as more derivatives of the type  $\text{M}(\text{CR})\text{X}_3$  were prepared, it became apparent that these "alkylidyne" complexes, in which the metal can be said to be in its highest possible oxidation state (6+), comprise a large and varied class, at least for Mo and W.

Evidence that related high-oxidation-state alkylidyne complexes<sup>3</sup> catalyze the olefin metathesis reaction<sup>4-6</sup> fueled speculation that some Mo or W alkylidyne complexes might catalyze the rare acetylene metathesis reaction (eq 1). We now know that some high-oxida-



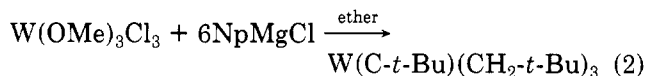
tion-state alkylidyne complexes do indeed catalyze the metathesis of acetylenes remarkably efficiently, and

Richard R. Schrock received his Ph.D. degree in 1971 from Harvard University. He then spent 1 year as an NSF Postdoctoral Fellow at Cambridge University, and 3 years at the Central Research and Development Department of E. I. duPont de Nemours and Company. Since 1975 he has been at the Massachusetts Institute of Technology where he is a Professor of Chemistry. His interests include synthetic and mechanistic organo-transition-metal chemistry, catalysis, reduction of carbon monoxide and molecular nitrogen, and applications to polymer synthesis. He was the recipient of the ACS Award in Organometallic Chemistry in 1985.

that some do not. We have begun to understand why. We also have begun to understand the relationship between alkylidyne complexes and complexes that contain other types of multiple bonds, such as metal-carbon double bonds,<sup>5,6</sup> metal-metal triple bonds,<sup>7</sup> or metal-nitrogen triple bonds.<sup>8</sup>

### Preparation of Alkylidyne Complexes

$\text{W}(\text{C}-t\text{-Bu})(\text{CH}_2-t\text{-Bu})_3$  can be prepared relatively simply in ~50% yield by adding  $\text{W}(\text{OME})_3\text{Cl}_3$  to 6 equiv of neopentylmagnesium chloride (eq 2).<sup>9</sup> The



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