

Table I. Reduction of Ketones in the Presence of Aldehydes<sup>a</sup>

| initial compound or mixture    | % reduction <sup>b</sup>                  |
|--------------------------------|---|
| hexanal                        | 2 (7) <sup>c</sup>                        |
| cyclohexanone                  | 100 (93) <sup>c</sup>                     |
| hexanal                        | 13  |
| 2-octanone                     | 96  |
| hexahydrobenzaldehyde          | 15  |
| cyclohexanone                  | 100                                       |
| hexahydrobenzaldehyde          | 22  |
| phenyl-2-propanone             | 93  |
| norbornenecarboxaldehyde       | 19  |
| 2-octanone                     | 90  |
| 1,2,5,6-tetrahydrobenzaldehyde | 14 <sup>c</sup>                           |
| acetophenone                   | 98 <sup>c</sup>                           |
| 1,2,5,6-tetrahydrobenzaldehyde | 14  |
| 5-nonanone                     | 48  |
| <b>1</b>                       | <b>2, 95<sup>d</sup> (78<sup>e</sup>)</b> |
| <b>3</b>                       | <b>4, 85<sup>d</sup> (75<sup>e</sup>)</b> |
| benzaldehyde                   | 60  |
| acetophenone                   | 100                                       |
| citral                         | 70  |
| 2-cyclohexenone                | 100                                       |

<sup>a</sup> The standard procedure is as follows. The two carbonyl compounds (1 mmol each)—or the dicarbonyl compound (2 mmol)—and 355 mg of  $\text{CeCl}_3 \cdot 6\text{H}_2\text{O}$  are dissolved in 6 mL of ethanol and 10 mL of water. The mixture is cooled to  $-15^\circ\text{C}$ , and then 60 mg of  $\text{NaBH}_4$  is added in one portion. Stirring is continued for 10 min. Excess  $\text{NaBH}_4$  is destroyed with 2 mL of acetone, and the mixture is then diluted with aqueous  $\text{NaCl}$  and extracted with ether. Usual workup of the ethereal layer affords a crude mixture which is analyzed and/or purified. <sup>b</sup> Identification of reduction products was made by comparison with authentic samples. Yields were calculated by VPC (Carlo Erba Fractovap, Carbowax column  $2.5 \times 2$  mm,  $\text{N}_2$  carrier). <sup>c</sup>  $\text{ErCl}_3 \cdot 5\text{H}_2\text{O}$  was used instead of  $\text{CeCl}_3 \cdot 6\text{H}_2\text{O}$ . <sup>d</sup> Yields of crude material were obtained by NMR analysis. <sup>e</sup> Isolated yields after column ( $\text{SiO}_2$ ) chromatography.

step, but at the same time allows the ready recovery of the aldehyde during the workup of the reaction mixture. This procedure represents the first *direct* solution to the problem of reverse selectivity and should find wide use in organic synthesis due to the ease of operation and exceptional rapidity.

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- (12) Lanthanoid ions strongly catalyze the reaction of  $\text{NaBH}_4$  with alcohols. An excess of the reducing agent is therefore necessary. The use of lesser amounts does not improve the selectivity.
- (13) The larger stabilization effect is observed with  $\text{Ce}^{3+}$ ,  $\text{Er}^{3+}$  which gives satisfactory results is followed by  $\text{Cr}^{3+}$ . The other ions tested gave poor selectivities.

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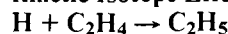
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#### An ab Initio Approach to Organic Reaction Rates. Kinetic Isotope Effects in the Reaction



Sir:

It is of general interest to predict rate constants of organic reactions entirely from a nonempirical standpoint. Recent advances in the ab initio energy gradient method<sup>1,2</sup> are expected to provide a reliable assistance to such predictions. We here report the results of a transition state theoretical (TST)<sup>3</sup> study, reinforced by the relevant ab initio molecular orbital computation, of the addition reaction  $\text{H} + \text{C}_2\text{H}_4 \rightarrow \text{C}_2\text{H}_5$ . The TST procedure, which would otherwise entail a considerable extent of empiricism on the transition state characteristics, has proved to be valuable indeed as a quantitative tool for kinetic considerations.

In the first place, geometries of ethylene and the transition state were optimized<sup>4</sup> by analytic evaluation of the potential energy gradients. The unrestricted Hartree-Fock (UHF) method with the 4-31 split-valence basis set<sup>5</sup> was used. The calculated barrier height for the reaction was 2.2<sub>0</sub> kcal/mol. The force constant matrices for both ethylene and the transition state were then constructed by numerical differentiation of the energy gradients.<sup>6</sup> The resultant normal mode

Table I. Comparison of the Experimental and the Present Theoretical Rate Constants  $k$  for the  $\text{H} + \text{C}_2\text{H}_4$  Reaction

| temp (T), K | $k$ ( $10^{-13}$ $\text{cm}^3$ molecule <sup>-1</sup> s <sup>-1</sup> ) |                   |
|-------------|---|-------------------|
|             | expt <sup>a</sup>   | theory, this work |
| 320         | 14.5 ± 1.1  | 16.9              |
| 298         | 11.3 ± 0.5 <sup>b</sup>   | 12.7              |
| 283         | 9.4 ± 0.6   | 10.3              |
| 258         | 6.3 ± 0.4   | 6.8               |
| 234         | 4.1 ± 0.2   | 4.3               |
| 216         | 3.0 ± 0.3   | 2.9               |
| 198         | 2.0 ± 0.1   | 1.8               |

<sup>a</sup>Reference 12. <sup>b</sup> Room-temperature values reported by other workers: 9.1 ± 0.9,<sup>7</sup> 12.2 ± 1.0,<sup>8</sup> 11.0 ± 1.3,<sup>9</sup> 12.5 ± 0.3,<sup>10</sup> and 11.0 ± 1.0.<sup>11</sup>

**Table II.** Calculated Rate Constants  $k$  ( $\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ ) for the Additions of Either H or D Atom toward a Series of Deuterated Ethylenes<sup>a</sup>

| ethylene                           | $10^{15}k$ (100 K) |      | $10^{13}k$ (200 K) |      | $10^{13}k$ (295 K) <sup>b</sup> |                  | $10^{12}k$ (400 K) |      |
|------------------------------------|--------------------|------|--------------------|------|---------------------------------|------------------|--------------------|------|
|                                    | H                  | D    | H                  | D    | H                               | D                | H                  | D    |
| $\text{CH}_2=\text{CH}_2$          | 0.70               | 1.19 | 1.87               | 1.84 | 12.2 (12.5 ± 0.4)               | 10.4 (8.7 ± 0.3) | 3.80               | 3.03 |
| $\text{CHD}=\text{CH}_2$           | 0.66               | 1.77 | 1.77               | 2.18 | 11.7                            | 11.6             | 3.67               | 3.30 |
| $\text{CD}_2=\text{CH}_2$          | 0.61               | 1.13 | 1.67               | 1.70 | 11.2                            | 9.8              | 3.55               | 2.90 |
| $\text{CHD}=\text{CHD}$<br>(cis)   | 0.60               | 1.10 | 1.67               | 1.69 | 11.2                            | 9.8              | 3.56               | 2.91 |
| $\text{CHD}=\text{CHD}$<br>(trans) | 0.58               | 1.06 | 1.65               | 1.67 | 11.1                            | 9.7              | 3.54               | 2.89 |
| $\text{CD}_2=\text{CHD}$           | 0.54               | 1.00 | 1.56               | 1.54 | 10.6                            | 9.3              | 3.44               | 2.82 |
| $\text{CD}_2=\text{CD}_2$          | 0.47               | 0.90 | 1.45               | 1.48 | 10.1 (11.5 ± 0.4)               | 8.9 (8.5 ± 0.5)  | 3.33               | 2.72 |

<sup>a</sup> All the entries are the total rate constants, i.e., the sum of the rate constants for the both ends of the ethylenic bond. <sup>b</sup> The values in parentheses are the experimental data.<sup>10</sup>

**Table III.** Positional Selectivity Ratios ( $k_\alpha/k_\beta$ ) as Functions of Temperature

| position<br>$\alpha$ $\beta$ | 100 K |      | 200 K |      | 295 K |      | 400 K |      |
|------------------------------|-------|------|-------|------|-------|------|-------|------|
|                              | H     | D    | H     | D    | H     | D    | H     | D    |
| $\text{CHD}=\text{CH}_2$     | 1.28  | 0.62 | 1.12  | 0.77 | 1.07  | 0.83 | 1.04  | 0.86 |
| $\text{CD}_2=\text{CH}_2$    | 1.55  | 1.62 | 1.22  | 1.24 | 1.12  | 1.13 | 1.07  | 1.08 |
| $\text{CD}_2=\text{CHD}$     | 1.24  | 1.27 | 1.10  | 1.11 | 1.06  | 1.06 | 1.03  | 1.03 |

frequencies (not listed here) are available on request. The zero-point vibrational energies were evaluated, to give the critical energy for reaction  $E_0 = 2.32$  kcal/mol.

On the basis of the geometries, energy, and vibrational frequencies obtained as above, the TST rate constants (with the transmission coefficient fixed at unity) were evaluated at various temperatures. The results are given in Table I, together with the reported experimental values.<sup>7-12</sup> The agreement between theory and experiment is excellent. One should note that previous hypothetical models<sup>10,13</sup> of the transition state have failed to reproduce the experimental data. In the temperature range 198–320 K, the Arrhenius  $A$  factor ( $\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ ) and the activation energy  $E_a$  (kcal/mol) obtained by the present calculation are  $\log A = -10.3$  and  $E_a = 2.31$ . The experimental results<sup>12</sup> are  $\log A = -10.4$  and  $E_a = 2.07$  in the same temperature range.

Encouraged by the above success, we have undertaken to examine kinetic isotope effects in the addition reaction in question. Various deuterium isotope combinations, both primary and secondary, were considered. The vibrational frequencies of the deuterated reactants as well as the transition states were calculated in exactly the same manner as for the nondeuterated case. The resulting rate constants are collected in Tables II and III. Experimental rate constants are available only for the additions of H and D to  $\text{C}_2\text{H}_4$  and  $\text{C}_2\text{D}_4$  at a few temperatures.<sup>10,14-17</sup> It is hoped that the present calculation constitutes a comprehensive prediction.

Tables II and III reveal the following.

**Relative Rates of H vs. D Additions.** At low temperatures, the D addition is predicted to be faster than the H addition because of a smaller  $E_0$  for the former.<sup>18</sup> As the temperature rises, the rate constants for the H addition increase more rapidly than do those for the D addition. A crossing over of the rates of H vs. D additions takes place at  $\sim 200$  K. Apparently, this is a consequence of a larger preexponential factor for the H addition, in which the translational part is a key factor.<sup>17</sup> The observed primary isotope effects in both  $\text{C}_2\text{H}_4$  and  $\text{C}_2\text{D}_4$  at 295 K<sup>10</sup> are well reproduced theoretically.

**Relative Rates of Deuterated Ethylenes.** For the H addition the rate constant decreases smoothly as the number of D atoms on the double bond increases, a trend which is in harmony with the experimental results for  $\text{C}_2\text{H}_4$  and  $\text{C}_2\text{D}_4$ .<sup>10</sup> The decrease in the rate upon deuteration is due to the decreasing preexponential factor (the rotational part in particular) as well as the

slightly increasing  $E_0$ . For the addition of a D atom, the effect of successive deuteration is somewhat complex.

**Geometrical Effects.** In both the H and D additions to  $\text{CHD}=\text{CHD}$ , the cis isomer is predicted to be very slightly more reactive, irrespective of the temperature, than its trans counterpart. The slight advantage of the cis isomer is due to its smaller  $E_0$ .<sup>19</sup> It deserves note in this context that, in radical additions of ethylene bearing nonisotopic substituents such as  $\text{CH}_3$ , F, and Cl, trans isomers are generally more reactive than the corresponding cis isomers.<sup>20</sup>

**Positional Reactivity.** Aside from the D addition to  $\text{CHD}=\text{CH}_2$ , both the H and D additions are predicted to take place preferentially at the more deuterated end of a double bond (Table III). The results are again contrasting to the general trend that the less substituted end is more reactive in olefins bearing a nonisotopic substituent.<sup>21</sup> The highest positional selectivity is seen in the addition to  $\text{CD}_2=\text{CH}_2$  and tends to be enhanced as the temperature falls. In fact, an ESR spectroscopic study<sup>22</sup> indicates that there exists a significant preponderance of H addition onto the  $\text{CD}_2$  end at 77 K. All the positional preferences given in Table III have stemmed primarily from the  $E_0$  factor.

In conclusion, the ab initio molecular orbital calculation seems to be capable of supplying sufficient information on the characteristics of the transition state for elementary reactions of moderately complex organic compounds. The importance of the entropy or preexponential factor in the rate processes should be emphasized in this connection. We plan to report more extensive treatments of organic rate processes elsewhere.

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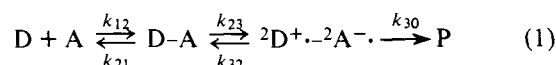
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### On the Correlation of the Kinetics of Electron-Transfer Processes with the Change in Reaction Free Energy. Application to Electron-Exchange-Initiated Chemiluminescence Reactions

Sir:

Single-electron-transfer reactions to generate radical-ion intermediates have been shown to be of crucial importance in the chemistry of organic and organometallic electronically excited states,<sup>1</sup> singlet oxygen,<sup>2</sup> radicals,<sup>3</sup> and organic peroxides.<sup>4</sup> The radical ions so produced have been observed to return to reactants (fluorescence quenching), to undergo further electron-transfer reactions that lead eventually to products, to combine to generate products, and to annihilate to form electronically excited states (chemiluminescence). Often the evidence for the involvement of radical-ion intermediates in these processes is a correlation of the observed rate constant for reaction with the one-electron oxidation or reduction potential of the reactant.<sup>5</sup> Our recent work on chemically initiated electron-exchange luminescence (CIEEL) has produced several such correlations.<sup>4e-i</sup> We report herein an interpretation of the kinetics of these apparently irreversible, endergonic, electron-transfer reactions based upon the model proposed by Weller and co-workers.<sup>6</sup>

Equation 1 is an adapted version of the general reaction scheme presented by Rehm and Weller:<sup>6b</sup>



The subscripts on the rate constants have been kept the same for consistency but the reactants have been generalized as

donor (D) and acceptor (A) and the electronic states of these are left unspecified. The products (P) of the reaction may be different electronic states of the reactants or new substances. The first equilibrium defines the diffusion of the reactants, the second the electron-transfer process. It should be noted also that the final step (rate constant  $k_{30}$ ) is irreversible and may correspond to diffusion apart of the ions or to chemical reaction. Application of the usual steady-state approximation to the concentration of encounter complex (D-A) and radical-ion pair ( ${}^2D^{+...-2}A^{-...}$ ) leads to

$$k_p = \frac{k_{30}k_{23}k_{12}}{(k_{32} + k_{30})(k_{21} + k_{23}) - k_{32}k_{23}} \quad (2)$$

(analogous to eq 2 of Rehm and Weller<sup>6b</sup>) which defines the rate constant for formation of P ( $k_p$ ). It is the correlation of this rate constant with the energetics of the electron transfer ( $\Delta G_{23}$ )<sup>7</sup> that can provide the kinetic evidence for an electron transfer in a reaction scheme. The relationship among the magnitudes of the various rate constants of eq 2 apparently determines the nature of this correlation. Weller and co-workers,<sup>6</sup> for example, have observed diffusion limited electron transfer for which  $k_p$  is independent of  $\Delta G_{23}$  (case i, below) and endergonic electron transfer for which  $k_p$  depends strongly on  $\Delta G_{23}$  (case ii, below). Our observations<sup>4e-i</sup> suggest a third form for the correlation of  $k_p$  with  $\Delta G_{23}$  (case iii, below) which occurs when the electron-transfer step is both endergonic and irreversible.

**Case i.** The electron-transfer step ( $k_{23}$ ) is exergonic ( $\Delta G_{23} < 0$ ) and irreversible. The two conditions specified above are not unrelated. The reverse electron transfer ( $k_{32}$ ) must be endergonic and therefore activated. Diffusion of the radical ions or chemical reaction ( $k_{30}$ ) could easily be orders of magnitude larger than  $k_{32}$ <sup>8</sup> ( $k_{32} \ll k_{30}$ ). Weller reports that, when  $\Delta G_{23}$  is negative by more than about 5 kcal/mol,  $k_p$  is equal approximately to the diffusion-limited rate constant  $k_{12}$ ; thus  $k_{23} \gg k_{21}$ . When these inequalities are applied to eq 2, they lead to the conclusion that, for this case, there should be no correlation between  $\Delta G_{23}$  and  $k_p$ . The slope of a semilog plot of  $k_p$  against  $\Delta G_{23}$  should be equal to zero, as has been seen experimentally.<sup>6a,b</sup>

**Case ii.** The electron-transfer step  $k_{23}$  is endergonic ( $\Delta G_{23} > 0$ ) and reversible. As in the above case, these two conditions are related. Back electron transfer ( $k_{32}$ ) is now the exergonic direction and since exergonic electron transfer competes effectively with diffusion  $k_{32} \gg k_{30}$ . By analogy,  $k_{23} \ll k_{21}$ . That is, diffusion is faster than activated electron transfer. When these inequalities are applied to eq 2, they lead to

$$k_p = k_{30}K_{12}K_{23} = k_{30}K_{12}e^{-\Delta G_{23}/RT} \quad (3)$$

where  $K_{12} = k_{12}/k_{21}$  and  $K_{23} = k_{23}/k_{32}$ . With these restrictions a semilog plot of  $k_p$  against  $\Delta G_{23}$  should give a line with a slope of  $-1/RT$ . Observation of this behavior, when  $\Delta G_{23}$  is represented as a linear function of the oxidation or reduction potential of the reactant, has been taken as strong evidence for the involvement of a rate-limiting electron-transfer step on the reaction coordinate.<sup>9</sup> Moreover, this observation tends to support the postulate of the model that  $K_{12}$  is independent of  $\Delta G_{23}$ . It should be noted that, when  $\Delta G_{23} \sim 0$ , the kinetics are apparently well fit by Weller's<sup>6b</sup> empirical equation and by Marcus' relationship.<sup>10</sup>

**Case iii.** The electron-transfer step ( $k_{23}$ ) is endergonic ( $\Delta G_{23} > 0$ ) and irreversible. As in case ii,  $k_{23} \ll k_{21}$  but now  $k_{32} \ll k_{30}$  as well. Such a circumstance might be realized if gain (or loss) of an electron by the reactant generated a reactive radical ion that underwent irreversible chemistry at a rate faster than the back electron transfer. Substitution of the above inequalities into eq 2 leads to

$$k_p = K_{12}k_{23} \quad (4)$$