

**Table I.** Application of Equation 2 to  $S_N2$  Transition Structures<sup>a</sup>

X	Y	$n_X$	$n_Y$	total bond order <sup>b</sup>
F	H	0.593	0.406	0.999
F	OH	0.546	0.455	1.001
F	CCH	0.491	0.510	1.001
F	NH <sub>2</sub>	0.591	0.421	1.012
F	CN	0.442	0.558	1.000
F	OOH	0.438	0.566	1.004
F	OCH <sub>3</sub>	0.509	0.492	1.001
H	NH <sub>2</sub>	0.482	0.513	0.995
H	OH	0.445	0.549	0.994
H	CCH	0.423	0.570	0.993
H	CN	0.389	0.610	0.999
HO	CN	0.426	0.583	1.009

<sup>a</sup> Calculated  $\alpha_X$  values (A) from eq 1 are as follows: H, 0.936; CCH, 0.959; CN, 0.948; NH<sub>2</sub>, 0.795; OH, 0.691; OCH<sub>3</sub>, 0.687; OOH, 0.703; F, 0.600. <sup>b</sup> Average value 1.001,  $\sigma_n = 0.004$ .

96.3 to 84.2°. This is the Bell-Evans-Polanyi-Leffler-Hammond effect:<sup>2,16</sup> *the more exothermic the reaction, the more closely the transition structure resembles the higher energy reactants.*

Linear fits to these data give, for Figure 2,  $r = 0.952$  and, for Figure 3,  $r = 0.976$ . Linear correlations have also been found for  $[X-CH_3-OH]^-$  transition states ( $R_{CO}$ ,  $r = 0.967$ ;  $\angle HCO$ ,  $r = 0.994$ ) and  $[X-CH_3-H]^-$  transition states ( $R_{CH}$ ,  $r = 0.977$ ;  $\angle HCH$ ,  $r = 0.996$ ). Such correlations suggest that these geometrical parameters of the transition structure are influenced more by the thermochemistry of the reaction than by electronic interactions between the entering and leaving groups.<sup>17</sup> It is particularly noteworthy that Figures 2 and 3 include cyanide/isocyanide, an "ambident nucleophile", and the "alpha-nucleophiles" hypofluorite and hydroperoxide. No unusual geometrical effects are observed with these nucleophiles.<sup>18</sup>

Our calculated geometries can also be employed to test the postulate of conservation of bond order along the reaction coordinate.<sup>19</sup> For an  $S_N2$  reaction, this corresponds to  $n_X + n_Y = 1$ , where  $n_X$  and  $n_Y$  are the bond orders of C-X and C-Y, respectively, and can be obtained from bond lengths using the Pauling relationship<sup>20</sup> (eq 1). The proportionality constants  $\alpha_X$

$$R - R_e = \alpha_X \ln(n_X) \quad (1)$$

were calculated from the transition structures for the degenerate reactions  $X^- + CH_3X \rightarrow CH_3X + X^-$ , in which  $n_X = 0.5$  and  $R_e$  is the C-X bond length in  $CH_3X$  (see footnote to Table I). In the cross-reactions  $X^- + CH_3Y \rightarrow CH_3X + Y^-$ , conservation of bond order requires that

$$n_X + n_Y = \exp[(R_{eX} - R_X)/\alpha_X] + \exp[(R_{eY} - R_Y)/\alpha_Y] = 1 \quad (2)$$

As can be seen in Table I, this behavior is observed uniformly in the transition structures.

The conservation of bond order in the transition state, coupled with the relations between reaction energy and bond length or bond angle, allows accurate estimation of transition-state geometries from properties of the reactants and products alone. These findings are being used successfully to extend the study of  $S_N2$  transition structures reported here.

**Acknowledgment.** This research has been supported by grants from the Natural Sciences and Engineering Research Council of Canada and the Petroleum Research Fund, administered by the American Chemical Society. We gratefully thank the Advisory

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**Supplementary Material Available:** Geometries and energies of all transition structures and ion-molecule complexes discussed in this and the following communication (6 pages). Ordering information is given on any current masthead page.

## Theoretical Studies of $S_N2$ Transition States. 2. Intrinsic Barriers, Rate-Equilibrium Relationships, and the Marcus Equation

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The reaction coordinate shown in Figure 1 for the gas-phase displacement  $X^- + CH_3Y \rightarrow XCH_3 + Y^-$  is characterized by two energy minima, corresponding to reactant (1) and product (3) ion-molecule clusters, separated by a central barrier (2), corresponding to the  $S_N2$  transition state. As discussed by Brauman and his co-workers,<sup>1</sup> such a reaction coordinate is consistent with the observation that the process proceeds at less than the collision rate, even when 2 has lower potential energy than the reactants, because partitioning of 1 in the direction of the reactants is favored entropically. With this interpretation, and model RRKM calculations, it has been found<sup>2</sup> that the energy difference between the reactants and the central barrier 2 (here termed  $\Delta E^*_{X,Y}$ ) can be correlated with the efficiency of the reaction.

Figure 2 shows a plot, based on 4-31G level calculations with full geometry optimization of all structures, of  $\Delta E^*_{X,Y}$  vs  $\Delta E^\circ$ , the calculated energy of reaction. No simple correlation between these quantities is apparent. That this is not an artifact of the computations may be seen from the experimental data of Bohme<sup>3</sup> and Brauman,<sup>2</sup> wherein reactions having similar  $\Delta H^\circ$  may proceed with very different efficiencies. Thus, although the geometries of  $S_N2$  transition states correlate well with the heats of reaction (the Bell-Evans-Polanyi-Leffler-Hammond effect<sup>4</sup>), their energies do not, and it must be concluded that the efficiency of a gas-phase  $S_N2$  reaction is not controlled solely by the enthalpy change.

The origin of such behavior has been treated in a number of rate-equilibrium relationships developed for elementary reactions,<sup>5,6</sup> which relate the reaction rate not only to  $\Delta E^\circ$  ( $\Delta G^\circ$ ) but also to certain intrinsic properties of the system. For an  $S_N2$  reaction these properties are associated with the nature of X and Y. The Marcus equation (eq 1) has already been applied suc-

$\Delta E^*_{X,Y} =$

$$\frac{1}{2}[\Delta E^*_{X,X} + \Delta E^*_{Y,Y}] + \frac{1}{2}\Delta E + \{(\Delta E)^2/8[\Delta E^*_{X,X} + \Delta E^*_{Y,Y}]\} \quad (1)$$

\* Fellow of the Alfred P. Sloan Foundation, 1981-1983.

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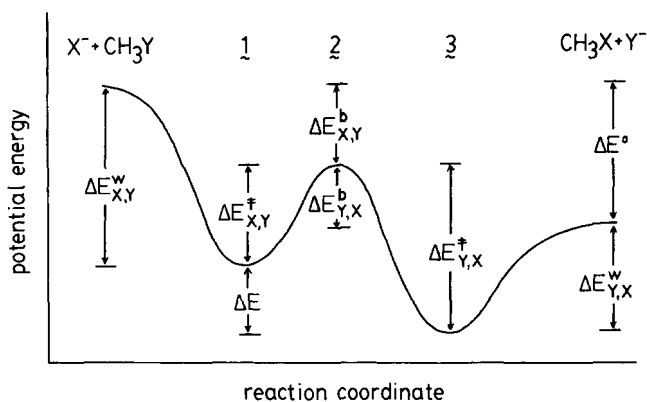
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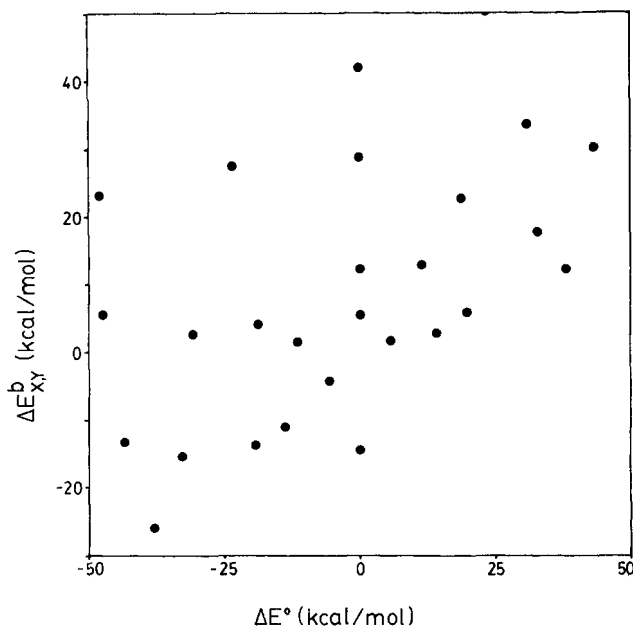
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**Figure 1.** Reaction coordinate for the gas-phase displacement reaction  $X^- + CH_3Y \rightarrow XCH_3 + Y^-$  and definitions of the quantities of eq 1-4.



**Figure 2.** Plot of calculated  $\Delta E_{X,Y}^b$  vs.  $\Delta E^\circ$  for combinations of X and Y including H, CCH, CN, NC, NH<sub>2</sub>, OH, OCH<sub>3</sub>, OF, OOH, F.

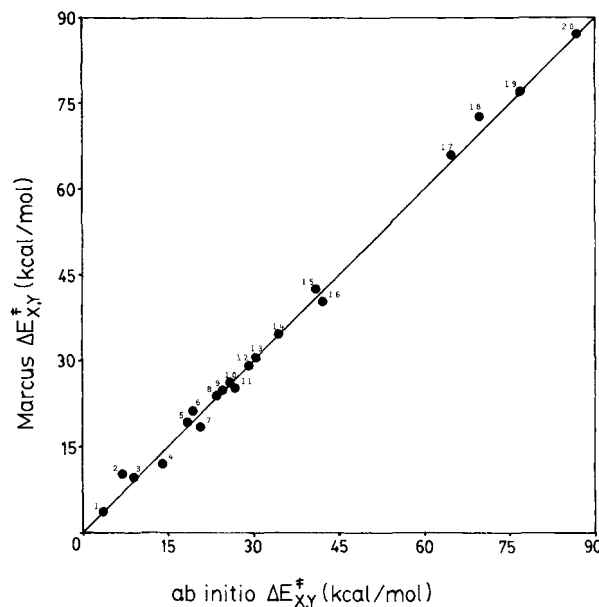
cessfully to the treatment of proton-transfer<sup>7</sup> and alkyl-transfer<sup>8</sup> reactions in solution and gas-phase ion-molecule reactions.<sup>9</sup> This equation relates  $\Delta E_{X,Y}^\ddagger$ , the barrier height for the cross-reaction of X displacing Y, to the energy change  $\Delta E$  and to the intrinsic barriers  $\Delta E_{X,X}^\ddagger$  and  $\Delta E_{Y,Y}^\ddagger$ . The Marcus equation is strictly applicable only to the process 1 → 2 → 3; consequently, the  $\Delta E$  term of eq 1 refers to the potential-energy difference between the reactant cluster 1 and the product cluster 2.

Table I lists a number of intrinsic barriers computed for degenerate S<sub>N</sub>2 reactions of the type  $X^- + CH_3X \rightarrow CH_3X + X^-$ . In each case the data have been obtained at the 4-31G level from the fully optimized geometries of 1 and 2. A number of factors influence the trends in  $\Delta E_{X,X}^\ddagger$ ; for example, charge delocalization onto the apical groups of 2 increases the  $X^-CH_3^+X^-$  resonance contribution and leads to a lower barrier.<sup>10,11</sup>

Figure 3 compares, for a number of combinations of X and Y,  $\Delta E_{X,Y}^\ddagger$  calculated from the energy difference between 1 and 2

**Table I.** Computed Intrinsic Barriers ( $\Delta E_{X,X}^\ddagger$ , kcal/mol) for Gas-Phase S<sub>N</sub>2 Reactions

X	$\Delta E_{X,X}^\ddagger$ , kcal/mol
H	57.3
HCC	50.4
NC	43.8
CH <sub>3</sub> O	23.5
HO	21.2
HOO	18.5
HS	15.6
F	11.7
Cl	5.5



**Figure 3.** Plot of  $\Delta E_{X,Y}^\ddagger$ , calculated directly from the energy differences between ion-molecule complexes and transition structures, vs. the same quantity from eq 1 for the reaction  $X^- + CH_3Y \rightarrow XCH_3 + Y^-$ . Data points 1-20 refer to the following (X,Y): (F,SH), (H,F), (HO,F), (F,OOH), (H,OH), (HCC,F), (HOO,F), (H,CN), (F,OH), (NC,F), (HO,CN), (F,CN), (HS,F), (H,CCH), (F,CCH), (NC,OH), (HO,H), (F,H), (HCC,H), (NC,H).

with the same quantity from the Marcus equation. The agreement is remarkable ( $\sigma_N = 1.0$  kcal/mol) and provides strong support for the suggestion<sup>9</sup> that gas-phase S<sub>N</sub>2 reactions can be interpreted with the aid of Marcus theory.

Expansion of the Marcus relationship, to permit a treatment of the entire reaction coordinate and, thus, allow a prediction of the experimentally more accessible quantity  $\Delta E_{X,Y}^b$ , is complicated by the different cluster well depths ( $\Delta E_{X,Y}^w$ ) associated with the different X and Y; these differences are caused by the different dipole moments and polarizabilities of the neutral molecules. This complication has been overcome by the observation that the sum of the reactant and product well depths in the exchange reaction is approximated very closely by the sum of the two intrinsic reaction well depths (eq 2).<sup>12</sup>

$$\Delta E_{X,Y}^w + \Delta E_{Y,X}^w \approx \Delta E_{X,X}^w + \Delta E_{Y,Y}^w \quad (2)$$

Incorporation of eq 2 into eq 1, and rearrangement of the resulting expression, leads to eq 3, which allows a prediction of

$$\Delta E_{X,Y}^b = \frac{1}{2}[\Delta E_{X,X}^b + \Delta E_{Y,Y}^b] + \frac{1}{2}\Delta E^\circ + \frac{(\Delta E)^2}{8[\Delta E_{X,X}^\ddagger + \Delta E_{Y,Y}^\ddagger]} \quad (3)$$

$\Delta E_{X,Y}^b$ . The quadratic term of eq 3 retains a dependence upon the cluster-to-cluster energy difference  $\Delta E$ . The further approximation, that  $\Delta E = \Delta E^\circ$ , leads to the modified Marcus re-

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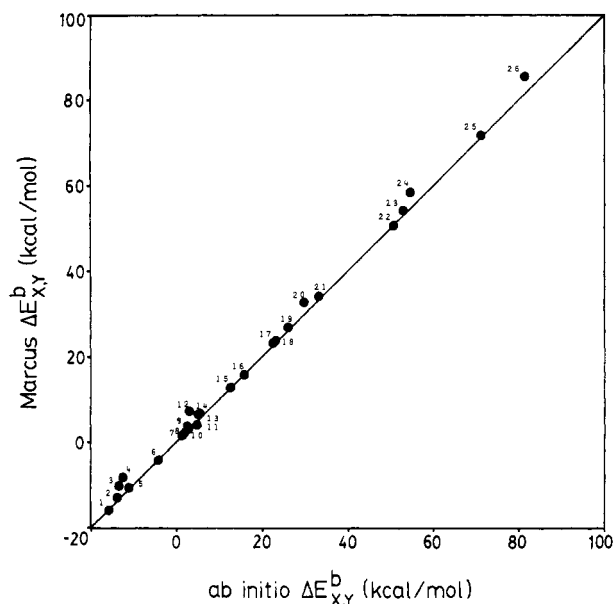
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(11) The intrinsic barrier trend  $NC^- > HO^- > F^- > Cl^-$  seen in Table I agrees with the experimental trend given for water solvent in Table II of ref 7b.

(12) The standard deviation between  $\Delta E_{X,Y}^w + \Delta E_{Y,X}^w$  and  $\Delta E_{X,X}^w + \Delta E_{Y,Y}^w$  for cross-reactions of H<sup>-</sup>, HCC<sup>-</sup>, NC<sup>-</sup>, F<sup>-</sup>, HO<sup>-</sup>, and HOO<sup>-</sup> is 0.95 kcal/mol.



**Figure 4.** Plot of  $\Delta E_{X,Y}^b$ , calculated directly from the energy difference between  $X^- + CH_3Y$  and the transition structure  $[X-CH_3-Y]^\ddagger$ , vs. the same quantity from eq 4. Data points 1-26 refer to the following (X,Y): (F,SH), (HO,F), (H<sub>2</sub>N,F), (H,F), (F,OOH), (CH<sub>3</sub>O,F), (F,CN), (F,O-CH<sub>3</sub>), (HO,CN), (HOO,F), (HCC,F), (H,CN), (H,OH), (F,OH), (NC,F), (HS,F), (F,CCH), (H,CCH), (H,NH<sub>2</sub>), (F,NH<sub>2</sub>), (NC,OH), (H<sub>2</sub>N,H), (HO,H), (F,H), (HCC,H), (NC,H).

lation shown in eq 4, from which the ion-molecule clusters have been eliminated.

$$\Delta E_{X,Y}^b \approx \frac{1}{2}[\Delta E_{X,X}^b + \Delta E_{Y,Y}^b] + \frac{1}{2}\Delta E^\circ + \frac{(\Delta E^\circ)^2}{8[\Delta E_{X,X}^* + \Delta E_{Y,Y}^*]} \quad (4)$$

Figure 4 compares  $\Delta E_{X,Y}^b$ , calculated from the energy difference between the reactants and **2**, with the values predicted by eq 4. Although the standard deviation of these results shows slightly more scatter ( $\sigma_N = 1.4$  kcal/mol) than the correlations of Figure 3, it seems clear that eq 4 is a useful rate-equilibrium relationship.<sup>13</sup>

A number of conclusions can therefore be stated: (1) the Marcus equation and its variants are of paramount importance for the treatment of rate-equilibrium data; (2) consequently, the concepts of nucleophilicity and leaving group ability become merged and absorbed into the intrinsic barriers and heats of reaction;<sup>8,9</sup> (3) a treatment of S<sub>N</sub>2 reactivity is thereby provided which is freed from the limitations of frontier molecular orbital theory;<sup>14</sup> (4) the gas-phase S<sub>N</sub>2 behavior of HOO<sup>-</sup> is entirely normal, as can be seen in Figures 3 and 4, as well as Figures 2 and 3 of ref. 4. The implications of these findings for interpretations of the  $\alpha$  effect<sup>15</sup> will be discussed elsewhere.

**Acknowledgment.** This research has been supported by grants from the Natural Sciences and Engineering Research Council of Canada and the Petroleum Research Fund, administered by the American Chemical Society. We gratefully thank the Advisory Research Committee of Queen's University and Wayne State University for generous allocation of computing funds.

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## Nucleophilic Activation of CO for Reduction by Hydrogen

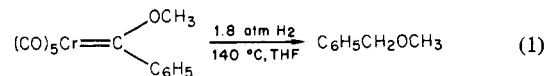
Kenneth M. Doxsee and Robert H. Grubbs\*

Contribution No. 6491 from the Laboratories of Chemistry  
California Institute of Technology  
Pasadena, California 91125

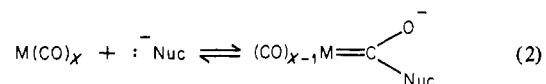
Received August 20, 1981

The production of chemicals from carbon monoxide and hydrogen feedstocks is a matter of intense current interest and vigorous investigation. Homogeneous transition-metal catalysts for this conversion are especially attractive, as they appear to offer promise of the selectivity and mechanistic simplicity which heterogeneous catalysts traditionally lack. Though the homogeneous hydrogenation of carbon monoxide has only recently been achieved,<sup>1,2</sup> the literature of the past few years abounds with reports of such reactions. The activation of carbon monoxide toward such homogeneous reduction by hydrogen has been approached in three ways: coordination of carbon monoxide to soluble transition-metal clusters,<sup>3</sup> coordination of Lewis acids to the oxygen atom of transition-metal bound carbon monoxide,<sup>2,4</sup> and either inter- or intramolecular donation of hydride to the carbonyl carbon atom.<sup>5</sup> We now wish to propose a new method of carbon monoxide activation toward homogeneous reduction and present experimental evidence demonstrating the utility of this approach in the production of functionalized organic products.

Fischer's pioneering work on the generation and isolation of transition-metal-carbene complexes,<sup>6</sup> coupled with Casey's report of the hydrogenation of such a complex<sup>7</sup> (reaction 1), suggested



that attack at carbonyl carbon by an external nucleophile could provide the activation of carbon monoxide required for reduction in the manner presented in reactions 2-7. This cocatalyst scheme



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