

MINDO/3 method predicts abnormally short C–F bonds and planar geometries for radicals known to be pyramidal. The latter trend may be an indirect consequence of the former. We conclude that the ab initio methods used in this work are more reliable for studying open-shell systems such as organic radicals.

It should be pointed out that ZDO methods may be inappropriate for studying problems where overlap repulsion plays a key role.^{26,27}

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Correlation between Exothermicity, Rate, and Negative Temperature Dependence in Slow Ion–Molecule Reactions

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Abstract: The rate constants (k_{450}) of 22 H^- transfer reactions between C_2 – C_7 carbonium ions and C_3 – C_{10} cyclic and acyclic hydrocarbons were measured. The values of k_{450} range between 2.2×10^{-9} and 3×10^{-13} $cm^3/mol\cdot s$, corresponding to collision efficiencies of approximately 1 to 10^{-4} . The rate constants exhibit large negative temperature coefficients of the form $k = AT^{-n}$, $n = 1.5$ – 6.8 . A direct relation between k_{450} and exothermicity is observed. An inverse linear correlation between $\ln k_{450}$ and the magnitude of the negative temperature coefficient (n) is also noted.

Introduction

The kinetics of slow hydride ion transfer reactions between carbonium ions and hydrocarbons were investigated in our laboratory in the past 3 years.^{1,2} In the course of our studies we observed that exothermic H^- transfer reactions exhibit unusually large negative temperature coefficients of the functional form $k = CT^{-n}$, $n = 1.5$ – 5.4 . It was demonstrated that activation energy is absent in one of the reactions, and it is plausibly absent in the remainder of these exothermic ion–molecule processes. In the present paper we shall discuss new observations concerning a correlation between the rate constants and the exothermicities of the transfer reactions. Another correlation of interest which we observed in H^- transfer reactions is the relation between the rate constants and their temperature coefficients. The present correlations are based on the kinetic data concerning 22 H^- transfer reactions. These data were obtained in part in previous work² and in part as the

result of new measurements which were executed in order to enlarge the data set which is the basis for the present correlations.

Experimental Section

The present work was carried out by pulsed, high-pressure mass spectrometry on The Rockefeller University Chemical Physics Mass Spectrometer. The experimental techniques used were identical with those described in previous publications.^{1,2} The hydrocarbons used were obtained from Chemical Samples Co., were of purity >98%, and were used without further purification.

Results

In this paper we present relations between rates, temperature coefficients, exothermicities, and structure for reactions between $C_2H_5^+$, *sec*- $C_3H_7^+$, and *t*- $C_4H_9^+$ and C_2 – C_7 hydrocarbons, for which kinetic data were obtained in the course of previous studies.⁷ In addition, we performed measurements

Table I. Rate Constants, Temperature Dependences, and Exothermicities of H⁻ Transfer Reactions: R₁⁺ + R₂H → R₂⁺ + R₁H

R ₁ ⁺	R ₂ H	-ΔH ^o , ^a kcal/ mol	k ₄₅₀ , ^b 10 ¹⁰ cm ³ / mol·s	n (in k = AT ⁻ⁿ)
1. C ₂ H ₅ ⁺		40	12	1.6
2. C ₂ H ₅ ⁺		42	15	0 ^c
3. C ₂ H ₅ ⁺		45	22	0 ^c
4.		18	2.5	2.0
5.		21	4.1	2.0
6.		23	9.5	2.5
7.		22	10	2.5
8.		—	12	2.5
9.		3.4	0.050	3.2
10.		5.4	0.11	4.5
11.		4.7	0.056	4.4
12.		6.9	0.27	2.7
13.		2.2	0.065	1.5
14.		1.3	0.011	5.4
15.			0.086	4.1
16.			0.0059	6.0
17.			0.0016	6.8
18.		1.5	0.0070	6.0
19.			0.0067	6.0
20.			0.0030	4.5
21.		1.8	0.011	3.7
22.		2.2	0.20	4.2

^a ΔH^o for reactions 1–5 is from data obtained by F. Lossing (private communication); for reactions 6–18 from data in ref 12–14; for reactions 21 and 22 from previously unpublished equilibrium data obtained in this laboratory. ^b Data for k₄₅₀ were mostly measured directly; in some cases, they were extrapolated from plots of ln k vs. ln T. Data are from ref 2 and from the present work. ^c These reactions proceed at about collision rate at 450 K, i.e., 450 K is below the transition temperature from "slow" to "fast" kinetics for these reactions.

on the reactions of the *t*-C₅H₁₁⁺ and *t*-C₆H₁₃⁺ with C₇–C₁₀ hydrocarbons and for reactions of the methylcyclopentyl ion with ethylcyclopentane and 1,2-dimethylcyclopentane. These measurements provide data on reactions with small exother-

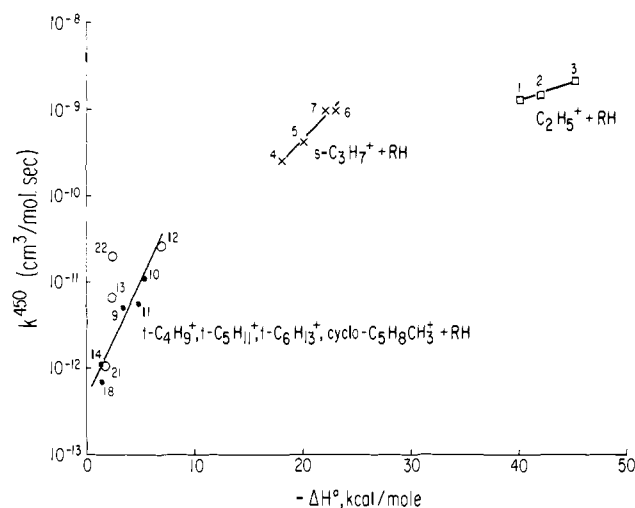


Figure 1. Correlation between exothermicities and rate constants in H⁻ transfer reactions. Note logarithmic scale of the ordinate. Circles represent reactions with cyclic reactants. Numbers indicate reactions as listed in Table I.

micity involving both highly branched and cyclic reactants. All the H⁻ transfer reactions for which kinetic data were obtained in our laboratory are listed in Table I. The table also shows the exothermicities of these reactions, the rate constant at 450 K, which is about the middle of the temperature range in most studies, and the magnitude of the negative temperature coefficient of *k*, i.e. *n* in the expression $k = AT^{-n}$.

Inspection of the data in Table I shows the great kinetic variability of H⁻ transfer reactions between carbonium ions and tertiary hydrocarbons. The reaction rate constants at 450 K span a range of about four orders of magnitude; i.e., collision efficiencies vary from 1 to about 1×10^{-4} . The temperature coefficients are also seen to vary widely from $T^{-1.5}$ to $T^{-6.8}$. The latter is by far the largest negative temperature dependence observed to date for a bimolecular exchange reaction in the gas phase. Inspection of the data also reveals these trends: As one proceeds from the highly exothermic reactions of the C₂H₅⁺ ion through the reactions of *sec*-C₃H₇⁺ to the slightly exothermic reactions of tertiary ions with more complex structures, the rate constant is seen to decrease and the temperature dependence is observed to become increasingly more negative.

The increase in rate constant with increasing exothermicity is clearly shown in Figure 1 throughout the entire set of reactions. In addition to this qualitative relationship, the data suggest that a more quantitative relationship might exist. Specifically, the plot of ln k₄₅₀ vs. -ΔH^o divides the reactions into three groups according to the nature of the reactant ion: C₂H₅⁺ (primary), *sec*-C₃H₇⁺ (secondary), and *t*-C₄H₉⁺, etc. (tertiary). Within each group, the correlation between k₄₅₀ and ΔH^o may be expressed by the equation

$$k = Ce^{-\beta \Delta H^o} \quad (1)$$

where *C* and β are constants which depend upon the nature of the reaction. A number of reservations are in order concerning the application of eq 1 to our data. We note that the number of points within each group of reactions is small. Also, the temperature coefficients of the reactions in Figure 1 vary from reaction to reaction (Table I). Since the rate constant in general correlates inversely with temperature coefficient, the slow reactions with lower exothermicities will get increasingly slower with increasing temperature. As a result, the plots in Figure 1 will get increasingly steeper with increasing *T*, i.e., β in eq 1 will increase with *T*. The degree of correlation in the plots of Figure 1 will also vary with temperature.

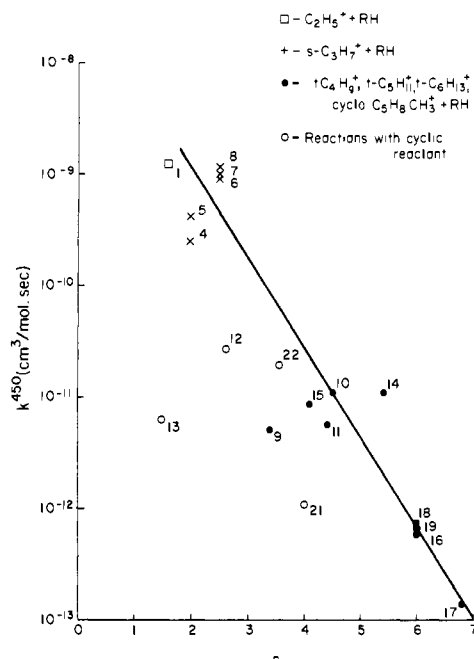


Figure 2. Correlation between temperature coefficients, i.e., n in $k = AT^{-n}$, and the rate constants. Circles represent reactions with cyclic reactants. Numbers indicate reactions as listed in Table I.

The other correlation of interest, one that is observed between $\ln k_{450}$ and the exponent of the temperature coefficient, is presented in Figure 2. Although a scattering of points is seen, a correlation is clearly noted. Statistical analysis shows a correlation coefficient¹⁶ of -0.79 between $\ln k$ and n for reactions which do not involve cyclic reactants. The case of cyclic reactants, which deviate from the correlation line, will be discussed separately.

Discussion

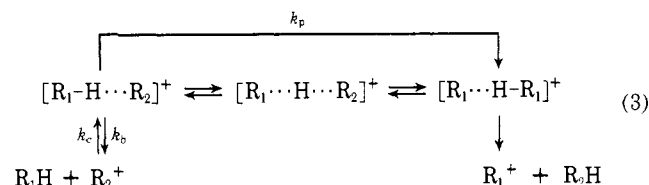
A correlation between exothermicities and activation energies was first reported by Polanyi for the reaction of the sodium atom with series of homologous alkyl halides.³⁻⁵ A linear relationship between the activation energy and exothermicity was found by Semenov⁶ to apply to an extensive set of substitution and addition reactions between radicals and molecules. Semenov expressed the Polanyi relation in the form

$$E_0 = A - \alpha q \quad (2)$$

where A is a constant for a series of homologous hydrocarbons, E_0 is the activation energy, and q is the exothermicity of the reaction. Cvetanovic⁷ found that a linear relation between activation energies and reaction exothermicities also applies in the reactions of oxygen atoms with olefins.

Even with the aforementioned reservations concerning the application of eq 1 in mind, it is interesting to compare our results with the Polanyi relation. For reactions with an Arrhenius behavior, i.e., $k = C \exp(-E_0/RT)$, the Polanyi relation (eq 2) yields $k = C \exp((-A + q)/RT) = C' \exp(\alpha q/RT)$. At a given temperature this expression has the same functional form as eq 1, with $\beta = \alpha/RT$. However, the Polanyi coefficient, α/RT , will decrease with increasing temperature, while the coefficient β should increase with increasing temperature, as noted above. We wish to suggest a possible, though speculative, rationalization of the similarity between the Polanyi relation (eq 2) for reactions with activation energies and our findings (eq 1) for reactions without activation energies. Farneth and Brauman⁸ suggested that slow ion-molecule reactions may involve internal barriers, which

are, however, lower than the energy of the separated reactants. Specifically, the following mechanism may apply:



Owing to ion-induced dipole interactions, and possibly also more specific bonding, the energy of all the intermediates is lower than the energy of $R_1H + R_2^+$. However, it is suggested that the energy of $[R_1 \cdots H \cdots R_2]^+$ is higher than that of $[R_1-H \cdots R_2]^+$ and of $[R_1 \cdots H-R_2]^+$. Thus a barrier to the forward reaction exists and RRK considerations suggest that this energy barrier will affect the magnitude of k_p . If this energy barrier decreases with increasing exothermicity in a set of homologous reactants, in a manner similar to the Polanyi relation, then k_p will increase correspondingly and the observed relation between k and $-\Delta H^\circ$ is accounted for.

In their work on the kinetics of slow ion-molecule reactions, Ausloos and Lias noted several instances of direct relation between exothermicity and rate constant for charge transfer reactions,^{9,10} four-center reactions between CX_3^+ and aldehydes and ketones,¹¹ as well as H^- transfer reactions involving CX_3^+ and series of homologous alkanes.¹² It thus appears that a relation between rate and exothermicity may be of some generality in ion-molecule kinetics.

The second relation of interest in the present data is that between rate constants and temperature coefficients (Figure 2). In previous publications^{1,2} we interpreted the negative temperature coefficients of H^- transfer reactions on the basis of transition state theory (TST) considerations, which led to the equation

$$k = CT^{-(2+r/2)} \quad (4)$$

Here r is the number of internal rotors in the reactants which become hindered upon the formation of the bimolecular reaction complex. We note that the TST considerations imply that the rate constant and its temperature coefficient should be correlated as follows. The functional form of our temperature coefficients is $k = AT^{-n}$. Comparing this result with eq 4, we observe that $n = (2 + r)/2$. As r increases, n increases, the magnitude of T^{-n} decreases, and k (eq 4) decreases. Thus we observe that for a series of reactions, other factors affecting the rate constant being comparable, TST considerations predict an inverse linear relation between $\ln k$ and r , such as is found in Figure 2.

For the reactions of acyclic reactants in Figure 2 we note that progressively slower reactions and higher values of n also involve progressively more complex reactants; i.e., the hindrance of an increasing number of internal rotors at the reaction center is becoming possible upon the formation of the reaction complex. Thus the relation observed in Figure 2 is consistent both with the functional form of the relation between $\ln k$ and n and with the qualitative relation between temperature coefficients, rate constants, and reactant structure, as predicted by TST.

The reactions involving cyclic reactants that were investigated in this work are slightly exothermic and correspondingly slow. However, in Figure 2 we note that these reactions exhibit significantly smaller temperature coefficients than reactions of acyclic reactants. These less negative temperature coefficients can be expected on the basis of TST arguments. Thus reactions of cyclic compounds, such as reactions 12, 21, and 22 (Table I), start with reactants with a total of only four, three, and three free internal rotors, respectively. This is, of course, the maximum number of rotors that can be hindered

upon the formation of the reaction complex. Thus the largest negative temperature coefficients that can be justified on the basis of the relation $n = (2 + r)/2$ for these reactions are T^{-4} , $T^{-3.5}$, and $T^{-3.5}$, respectively. On the other hand, the total numbers of internal rotors in reactions 10, 11, 14, and 18 are 8, 9, 10 and 11 (some of these may already be hindered in the neutral reactants). Temperature coefficients as large as T^{-6} – $T^{-7.5}$ could therefore be explained for these reactions, although it may be difficult, for example, to hinder seven rotors upon the formation of the transition complex from the reactants of reaction 14. The small temperature coefficient of $T^{-1.5}$ for reaction 13 can be justified on the basis that there are no free rotors in norbornane; in fact, TST requires that $r = -1$ in this case, i.e., a new rotor has to be formed in the complex in this reaction. Indeed, a new internal rotation can be seen around the bond ($\text{CH}_3)_3\text{C}^+ \cdots \text{H}-\text{C}(\text{C}_6\text{H}_{11})$ in the reaction complex. The simple TST relation of eq 4 is therefore consistent with the temperature dependences that we observe in the present set of reactions. We note that none of the 22 reactions examined shows a temperature coefficient large enough to rule out its rationalization on the basis of TST, i.e., eq 4. This is encouraging, since some reactions were studied specifically to test for this possibility. Thus a temperature coefficient of T^{-10} in any of the open-chain reactant cases, or as high as T^{-5} in the cyclic reactants, would have required the postulation of more hindered rotors in the reaction complexes than could possibly be accounted for in these reactions.

In summary, increasing exothermicity is observed to correlate with increasing rate constant throughout the set of 22 H^- transfer reactions that we observed. We also observe a trend of increasingly large negative temperature coefficients associated with decreasing rate constants and with increasing complexity of the reactants. The latter relations are justified by TST consideration. However, the relation between ex-

othermicities and rate constants cannot be justified by the simple TST relation of eq 4. This relation may reflect the variation of internal energy barriers with the variation of exothermicities in a Polanyi-type relationship. In turn, the effect of the variation of internal energy barriers on the rate constants can be justified by the application of unimolecular dissociation theory to the reactions of the reaction complex, along the line suggested by Farneth and Brauman.⁸ We note that the application of TST and unimolecular dissociation theory concepts to slow ion–molecule reactions is not incompatible, since both the entropy of the reaction complex and internal energy barriers associated with this complex will affect the rate constant and its temperature dependence.

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Theoretical Studies of Thermal Rearrangements. Methylene cyclopropane and Barriers to Internal Rotation in Biradicals

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Abstract: The surface for the degenerate thermal rearrangement of methylenecyclopropane has been investigated by a molecular orbital method (PRDDO). Optimized geometries are presented for methylenecyclopropane and for three forms of trimethylenemethane: D_{3h} triplet, C_{2v} perpendicular singlet, and C_{2v} planar singlet. The C_{2v} perpendicular singlet is stable by 1.8 kcal/mol over the planar C_{2v} singlet state. The maximum calculated activation energy, 47.7 kcal/mol is in reasonable agreement with the experimental activation energy of 40.1 kcal/mol for a similar rearrangement. The barrier to ring closure is approximately <3.3 kcal/mol. A low-energy path was found having a barrier of 2.8 kcal/mol for permutation of the unique methylene group. The barriers to internal rotation in the singlet states of two isomeric bisallyl molecules (2,2' and 2,4) are 2.1 and 2.6 kcal/mol, respectively. These low barriers to rotation are important in explaining the racemization observed in the thermal rearrangements of optically active, substituted methylenecyclopropanes and 1,2-dimethylenecyclobutanes.

Introduction

The interaction of radical centers on the same molecule is important in understanding the potential energy surfaces for thermal rearrangements of small organic molecules. A suitably

simple system is methylenecyclopropane. Rearrangements of substituted methylenecyclopropanes have been the focus of numerous experimental studies and some theoretical work. Ullman¹ found that some chirality was retained in the thermal rearrangement of Feist's ester, 1. Doering and Roth² showed that the rearrangement of **1** proceeded with inversion of con-

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