

See discussions, stats, and author profiles for this publication at: <https://www.researchgate.net/publication/231401075>

Entropy-driven proton-transfer reactions

ARTICLE *in* THE JOURNAL OF PHYSICAL CHEMISTRY · AUGUST 1991

Impact Factor: 2.78 · DOI: 10.1021/j100170a039

CITATIONS

30

READS

11

1 AUTHOR:



[Michael Noah Mautner](#)

Virginia Commonwealth University

202 PUBLICATIONS 5,307 CITATIONS

SEE PROFILE

conclusion is that at least for some compositions the mechanism of the Belousov-Zhabotinsky reaction apparently includes some steps that are virtually diffusion controlled and probably of radical-radical type whether the Radicalator model is valid in detail or not.

(ii) Diffusion-controlled reactions can cause hitherto unsuspected stirring effects even in batch reactors. Conversely, a stirring effect observed in a batch or a continuously fed stirred tank reactor can indicate the presence of a diffusion-controlled reaction. The reactants of such a reaction are not necessarily radicals, but both reactants should be present in low concentrations (10^{-6} M or less) and the diffusion-controlled step should play an important role in the whole mechanism.

(iii) A uniform ultrasonic stirring can substitute for the conventional mechanical stirring in experiments with the BZ reaction. This is important in the case of delicate nonlinear dynamic experiments⁴⁹ (observation of different bifurcations,^{36,50,51} strange

attractors,⁴⁹ etc.) where the nonuniform mechanical stirring can create different reaction zones⁵² within the otherwise uniform reactor. (The rate of a diffusion-controlled reaction⁴⁰ would be higher at the stirring propeller than at the wall of the reactor.⁵³)

Acknowledgment. We thank Prof. H. D. Försterling, Prof. H. L. Swinney, and I. Noszticzius for their help in computer hardware and software and M. Noszticzius and E. Kovács for their help in preparing the manuscript. This work was partially supported by the Department of Energy Office of Basic Energy Sciences, the Robert A. Welch foundation, and OTKA grants.

Registry No. BrO_3^- , 15541-45-4; Ce, 7440-45-1; malonic acid, 141-82-2.

(49) (a) Swinney, H. L.; Roux, J. C. In *Nonequilibrium Dynamics in Chemical Systems*; Vidal, C., Pacault, A., Eds.; Springer: Berlin, 1984; p 124. (b) Noszticzius, Z.; McCormick, W. D.; Swinney, H. L. *J. Phys. Chem.* **1989**, *93*, 2796. (c) Argoul, F.; Arneodo, A.; Richetti, P.; Roux, J. C.; Swinney, H. L. *Acc. Chem. Res.* **1987**, *20*, 436.

(50) Bar-Eli, K.; Noyes, R. M. *J. Chem. Phys.* **1987**, *86*, 1927.
(51) Gáspár, V.; Showalter, K. *J. Chem. Phys.* **1988**, *88*, 778.
(52) Györgyi, L.; Field, R. J. *J. Phys. Chem.* **1989**, *93*, 2865.
(53) Nagata, S. *Mixing*; Wiley: New York, 1975; Figures 3.32 and 3.35.
(54) Some new features of stirring sensitivities of the BZ reaction were reported just recently: Lopez-Tomas, L.; Sagues, F. *J. Phys. Chem.* **1991**, *95*, 701.

Entropy-Driven Proton-Transfer Reactions

Michael Meot-Ner (Mautner)

Chemical Kinetics Division, National Institute of Standards and Technology, Gaithersburg, Maryland 20899
(Received: February 14, 1991)

The relation between kinetics and thermochemistry in fast reactions is examined, including reactions with substantial entropy changes. Rate constants for such reactions, in the range of $(0.02-3.0) \times 10^{-9} \text{ cm}^2 \text{ s}^{-1}$, were measured by pulsed high-pressure mass spectrometry. The following relations were observed: (1) The reaction efficiency in either direction is controlled uniquely and completely by the overall reaction free energy change. Specifically, the efficiency r is determined by the equilibrium constant according to $r = K/(1 + K)$. (2) The sum of reaction efficiencies in the forward (exergonic) and reverse (endergonic) directions is near unity ($r_f + r_r \approx 1$). These relations are observed in anionic and cationic systems, in reactions with ΔH° up to 12 kcal/mol and with ΔS° up to 15 cal/(mol K). Consistent with (1), reactions that are endothermic up to 7 kcal/mol can nevertheless proceed near the collision rate, when positive entropy changes make the reactions exergonic. The entropy changes are effective regardless of their structural origin. Relations analogous to (1) and (2) are also derived for reactions with multiple channels that proceed without significant barriers through a common intermediate.

Introduction

Most fast ion-molecule reactions are exothermic processes with negligible entropy changes. However, some bimolecular exchange reactions do involve substantial entropy changes, and even small entropy changes can have significant effects at high temperatures. It is necessary therefore to generalize the relation between kinetics and thermochemistry in fast ion-molecule reactions, to include reactions with significant entropy changes. This is the objective of the present work.

Usually, fast ion-molecule reactions proceed in the exothermic (and exergonic) direction near the collision rate, i.e., $k = k_{\text{coll}}$. In other words, the reaction efficiency is near unity, eq 1.

$$r = k/k_{\text{coll}} \approx 1 \quad (1)$$

In the reverse direction these processes are slowed by the thermochemical factor, eq 2.

$$k = k_{\text{coll}} \exp(-\Delta G^\circ/RT) = k_{\text{coll}} \exp(-\Delta H^\circ/RT) \quad (2)$$

Bohme demonstrated these relations for a set of reactions,¹ and they are accurate for reactions with substantial overall free energy

changes, i.e. where $|\Delta G^\circ| > 4 \text{ kcal/mol}$. However, for a general treatment, fast reactions with small overall free energy changes should be also examined. This paper will focus on a set of such reactions.

The reactions in Bohme's study had small entropy changes and ΔG° and ΔH° were indistinguishable within the accuracy of the thermochemical data.² We observed, however, some proton-transfer and charge-transfer reactions with large entropy changes, up to 15 cal/(mol K).^{3,4} In these cases the kinetics were clearly determined by ΔG° rather than ΔH° . This was evident in particular when the magnitude of $T\Delta S^\circ$ was large and ΔH° and ΔG° had opposite signs. In particular, we found endothermic reactions that proceeded near unit efficiency even when the enthalpy factor of $\exp(-\Delta H^\circ/RT)$ would reduce the efficiency by 5 orders of magnitude. This occurred where $T\Delta S^\circ$ was positive and large enough to render ΔG° negative.^{3,4}

(2) Henchman, M. In *Structure, Reactivity and Thermochemistry of Ions*; Ausloos, P., Lias, S. G., Eds.; Reidel: Dordrecht, The Netherlands, 1987; p 381.

(3) Meot-Ner (Mautner), M.; Hamlet, P.; Hunter, E. P.; Field, F. H. *J. Am. Chem. Soc.* **1980**, *102*, 6393.

(4) Sieck, L. W.; Meot-Ner (Mautner), M. *J. Phys. Chem.* **1982**, *86*, 3646. Meot-Ner (Mautner), M. In *Structure, Reactivity and Thermochemistry of Ions*; Ausloos, P., Lias, S. G., Eds.; Reidel: Dordrecht, The Netherlands, 1987; p 383.

(1) (a) Bohme, D.; Mackay, G. I.; Schiff, H. I. *J. Chem. Phys.* **1980**, *73*, 4976. (b) Bohme, D. In *Ionic Processes in the Gas Phase*; Altmeyer-Ferreira, M. A., Ed.; Reidel: Dordrecht, The Netherlands, 1984; p 111.

Unit collision efficiency means that all collisions lead to the products. More generally, we observed that fast reactions obey relations 3 and 4. These relations can be derived from a simple

$$r_f + r_r \approx 1 \quad (3)$$

$$r = K/(1 + K) \quad (4)$$

kinetic model based on the fact that there occurs no reflection from barriers along the reaction path (which would decrease the efficiency below unity).⁴

Here r_f and r_r are the reaction efficiencies in the forward and reverse directions, respectively. (The exergonic direction will be considered as the "forward" direction. Note that reaction in the reverse, endergonic direction is slower than the collision rate, but only to the extent determined by the overall equilibrium constant K according to (4), without being slowed by other factors. In other words, not only the reaction in the exergonic direction but that in the endergonic direction as well, is as fast as possible. In this sense these reactions, in both directions, may be called "intrinsically fast".) K is the equilibrium constant written in either direction, and r is the reaction efficiency in that direction.

Equation 3 may be seen as the general definition of fast kinetics. Equation 4 shows that the efficiencies of such reactions are determined completely and uniquely by the equilibrium constant. We verified eqs 3 and 4 experimentally in reactions with various enthalpy and entropy changes, where K ranged over 3 orders of magnitude and the reaction efficiencies ranged from 0.01 to 1.⁴ Equations 3 and 4 also apply for larger values of ΔG° where they reduce to (1) and (2), respectively.

To date, fast reactions with large entropy changes were demonstrated only in a small set of cationic reactions, and structurally with only one type of entropy change, which involves cyclic ion structures. The present paper will further generalize these observations. Experimental data will show that relations 3 and 4 apply for fast reactions of anions as well as cations, with substantial entropy changes due to various structural factors. The formal kinetic treatment will be also generalized to intrinsically fast reactions with several channels, following a recent suggestion by Lifshitz.⁵

Experimental Section

The measurements were performed on the NIST pulsed high-pressure mass spectrometer, using standard techniques.⁶

In the pulsed measurements, fast chemical ionization processes produced the reactant ions within the time of the ionizing pulse, about 0.5–1 ms. Approach to equilibrium occurred during the following 0.1–2 ms and equilibrium was observed for 1–2 ms. An example is shown in Figure 1. Values of ΔH° and ΔS° were obtained from van't Hoff plots. The equilibrium results are presented in detail elsewhere.^{7,8}

For cationic systems, CH_4 or C_6H_{12} were used as carrier gases, with the reactants added as 0.01–0.0001% of the mixture. For anionic systems the mixtures also included trace N_2O or CH_3ONO for electron capture. The total source pressures were 0.4–2 torr. The compounds were of commercial sources with nominal purities greater than 98% and used as purchased. The reaction mixtures were prepared in a glass bulb heated to 150 °C, and were allowed to flow to the ion source through glass and stainless steel lines also heated to about 150 °C.

Results

Rate constants were obtained in most of the present measurements from approach to equilibrium. Examples of temporal ion profiles are shown in Figure 1.

In most reactions, the conditions were optimized for equilibrium rather than kinetic studies. In particular, the reactant concen-

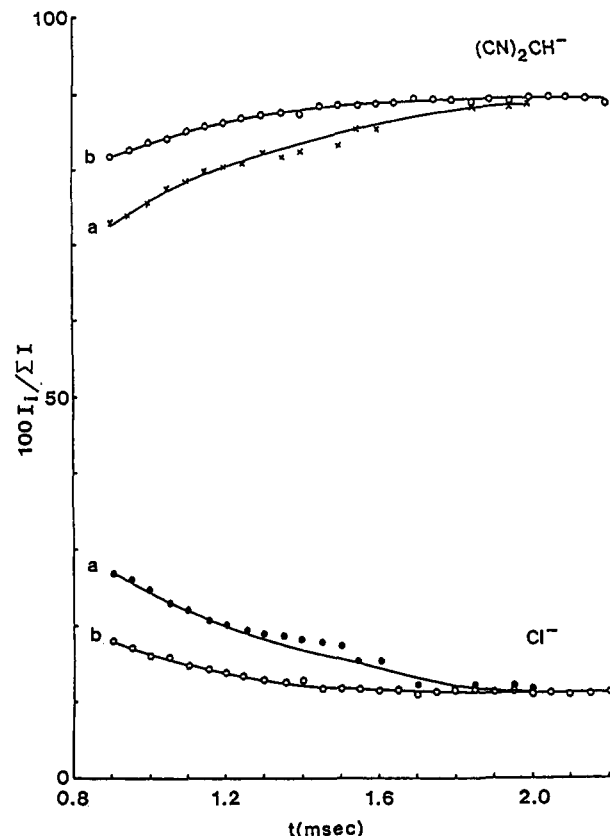


Figure 1. Temporal profiles of normalized ion intensities following an ionizing pulse of 0.8 ms, in the reaction $\text{Cl}^- + \text{H}_2\text{C}(\text{CN})_2 \rightarrow \text{HC}(\text{CN})_2^- + \text{HCl}$, with 0.012% $\text{H}_2\text{C}(\text{CN})_2$ and 0.0056% HCl in CH_4 at 613 K: (a) $P = 0.82$ Torr; (b) $P = 1.44$ Torr. The rate constants from both (a) and (b) are $k_f = 1.2$ and $k_r = 0.2 \times 10^{-9} \text{ cm}^3 \text{ s}^{-1}$.

trations were high to assure that equilibrium was reached. This resulted in fast approach to equilibrium, and the kinetics could be observed for relatively short times under conditions where most of the reactants were already converted to products. These features are noted in Figure 1. For this reason, and also on the basis of reproducibility, the error of the reported rate constants is estimated as $\pm 30\%$. As usual, checks were made to ensure that the equilibrium constants and rate constants were independent of mixture composition and ion source pressure. As a further check on the kinetic measurements, rate constants for a selected system, $\text{Cl}^- + \text{H}_2\text{C}(\text{CN})_2$, were measured both under reversible and irreversible conditions. Irreversible kinetics were measured in the absence of the neutral reactant HCl , by generating Cl^- from trace CCl_4 . A comprehensive study of this reaction will be presented elsewhere.⁹

Rate constants, reaction efficiencies, and thermochemical parameters for 15 reactions are shown in Table I. All the results are from the present work, except for reactions 1 and 2, which are quoted because they illustrate the entropy effects in very simple model systems.^{10,11}

Discussion

1. Kinetic Features. The essential features of fast kinetics are expressed by eqs 3 and 4 above. The derivation, for the general case of multiple channels, will be presented below, but first we shall observe these relations experimentally in the data in Table I.

a. Overall Efficiency. Equation 4 predicts that in significantly exergonic ($K \gg 1$) fast reactions the efficiency is near unity, while in the reverse direction the efficiency is small, i.e. $r = K_r =$

(5) Iraqi, M.; Petrank, A.; Peres, M.; Lifshitz, C. *Int. J. Mass Spectrom. Ion Processes*, in press. Lifshitz, C. Personal communication.

(6) Meot-Ner (Mautner), M.; Sieck, L. W. *J. Am. Chem. Soc.* **1983**, *105*, 2956.

(7) Meot-Ner (Mautner), M.; Kafafi, S. A. *J. Am. Chem. Soc.* **1988**, *110*, 6297.

(8) Meot-Ner (Mautner), M.; Sieck, L. W. *J. Phys. Chem.* **1990**, *94*, 7730.

(9) Meot-Ner (Mautner), M.; Tsang, W. J. Unpublished results, in preparation.

(10) Henchman, M. J.; Adams, N. D.; Smith, D. *J. Chem. Phys.* **1981**, *75*, 1201.

(11) Smith, D.; Adams, N. G.; Alge, E. *J. Chem. Phys.* **1982**, *77*, 1261.

TABLE I: Kinetics and Thermochemistry of Fast Reactions

	k^a	r^b	$K/(1+K)$	$e^{-(\Delta H^\circ/RT)}$	$E_a^{c,d}$	ΔH°^c	ΔS°^c	ΔG°^c	T, K	type
Isotope Exchange										
1f $D^+ + HD \rightarrow H^+ + D_2$	1.2	0.63	0.85	>1	-0.3	-1.0	-1.6	-0.7	205	entropy-inhibited
	0.95	0.50	0.70	>1				-0.5	295	entropy-inhibited
1r $H^+ + D_2 \rightarrow D^+ + HD$	0.21	0.09	0.15	0.09	0.7	1.0	1.6	0.7	205	
	0.36	0.16	0.30	0.18				0.5	295	
2f $D^+ + H_2 \rightarrow H^+ + HD$	2.2	1.05	0.95	>1	-0.3	-0.9	1.4	-1.2	205	fast exothermic
	1.7	0.81	0.90	>1				-1.3	295	fast exothermic
2r $H^+ + HD \rightarrow D^+ + H_2$	0.11	0.06	0.05	0.11	0.6	0.9	-1.4	1.2	205	entropy-inhibited
	0.17	0.07	0.10	0.22				1.3	295	entropy-inhibited
Cationic Proton Transfer $AH^+ + B \rightarrow BH^+ + A$										
3f $CH_3CO(CH_2)_2COCH_3H^+ + 2\text{-Fpyridine}$	1.1	0.57	0.85	0.083		2.6	8.5	-1.8	523	entropy-driven
3r $2\text{-Fpyridine}H^+ + CH_3CO(CH_2)_2COCH_3$	0.19	0.06	0.15	>1		-2.6	-8.5	1.8	523	entropy-inhibited
4f $CH_3CONHCH_2COOCH_3H^+ + 2\text{-Fpyridine}$	1.8	0.94	0.70	0.0028		7.0	13.4	-1.0	597	entropy-driven
	1.8	0.90	0.52	0.0012				-0.1	523	entropy-driven
4r $2\text{-Fpyridine}H^+ + CH_3CONHCH_2COOCH_3$	0.78	0.34	0.30	>1	-7.9	-7.0	-13.4	1.0	597	entropy-inhibited
	1.64	0.68	0.48	>1				0.1	523	entropy-driven
5f $2\text{-Fpyridine}H^+ + CH_3CONHCH(CH_3)COOCH_3H^+$	1.2	0.52	0.96	>1		-12.2	-14.7	-3.6	585	fast exothermic
	1.2	0.51	0.98	>1				-4.2	544	fast exothermic
5r $CH_3CONHCH(CH_3)COOCH_3H^+ + 2\text{-Fpyridine}$	0.054	0.03	0.04	0.000029	12.6	12.2	14.7	3.6	585	entropy-enhanced
	0.024	0.01	0.02	0.000013				4.2	544	entropy-enhanced
Cationic Charge Transfer $A^+ + B \rightarrow B^+ + A$										
6f $C_6H_6^+ + C_6H_5F$	0.73	0.52	0.62	>1		-1.2	-2.1	-0.4	355	fast exothermic
6r $C_6H_5F^+ + C_6H_6$	0.68	0.40	0.38	0.21		1.1	2.1	0.4	355	entropy-enhanced
Anionic Proton Transfer $A^- + BH \rightarrow B^- + AH$										
7f $Cl^- + H_2C(CN)_2$	1.3	0.44	0.89	0.15		2.3	8.0	-2.5	596	entropy-driven
	1.6	0.48	0.81	0.075				-1.3	444	entropy-driven
7r $HC(CN)_2^- + HCl$	0.17	0.15	0.11	>1	-2.6	-2.3	-8.0	2.5	596	entropy-inhibited
	0.41	0.34	0.19	>1				1.3	444	entropy-inhibited
8f $OH^- + \text{naphthalene}$	1.8	0.82	0.95	0.10		2.9	10.5	-3.7	632	entropy-driven
	1.8	0.82	0.93	0.072				-2.9	552	entropy-driven
8r $(\text{naphthalene} - H)^- + H_2O$	0.09	0.06	0.05	>1	-2.5	-2.9	-10.5	3.7	632	entropy-inhibited
	0.12	0.07	0.07	>1				2.9	552	entropy-inhibited
9f $C_6H_4F^- + CH_3OH$	1.51	1.00	0.66	>1		-5.7	-8.0	-0.8	618	fast exothermic
9r $CH_3O^- + C_6H_5F$	0.79	0.41	0.34	0.0099		5.7	8.0	0.8	618	entropy-enhanced
10f $CH_3O^- + C_6H_5CN$	3.0	0.86	0.95	0.24		1.8	8.9	-3.8	624	entropy-driven
10r $C_6H_4CN^- + CH_3OH$	0.14	0.10	0.05	>1		-1.8	-8.9	3.8	624	entropy-inhibited
11f $CH_3O^- + \text{quinoline}$	0.64	0.26	0.60	0.044		3.7	7.0	-0.5	593	entropy-enhanced
	0.20	0.08	0.45	0.025				0.2	501	entropy-enhanced
11r $(\text{quinoline} - H)^- + CH_3OH$	0.40	0.28	0.40	>1		-3.7	-7.0	0.5	593	entropy-inhibited
	0.28	0.10	0.55	>1				-0.2	501	entropy-inhibited
12f $CH_3O^- + H_2CCCH_2$	1.80	0.76	0.85	0.14		2.5	7.4	-2.2	640	entropy-driven
12r $H_2CCCH^- + CH_3OH$	0.45	0.26	0.15	>1		-2.5	-7.4	2.2	640	entropy-inhibited
13f $CH_3O^- + C_6H_5CH_3$	1.05	0.60	0.84	0.17		2.3	6.9	-2.1	643	entropy-driven
13r $C_6H_5CH_2^- + CH_3OH$	0.12	0.08	0.16	>1		-2.3	-6.9	2.1	643	entropy-inhibited
14f $OH^- + 1,4\text{-diazine}$	2.2	1.1	0.96	0.20		2.1	9.6	-4.1	646	entropy-driven
	2.2	1.1	0.95	0.14				-3.0	529	entropy-driven
14r $(1,4\text{-diazine} - H)^- + H_2O$	0.09	0.05	0.04	>1	-1.7	-2.1	-9.6	4.1	646	entropy-inhibited
	0.12	0.07	0.05	>1				3.0	529	entropy-inhibited
15f $SH^- + HCN$	1.8	0.67	0.93	0.85		0.2	5.8	-3.2	603	entropy-driven
	1.8	0.60	0.94	0.81				-2.6	481	entropy-driven
15r $CN^- + H_2S$	0.12	0.09	0.07	>1	0.0	-0.2	-5.8	3.2	603	entropy-inhibited
	0.12	0.08	0.06	>1				2.6	481	entropy-inhibited

^a $10^{-9} \text{ cm}^3 \text{ s}^{-1}$. ^b Efficiency $r = k/k_{\text{coll}}$. The collision rate is calculated according to ref 12. ^c ΔH° , ΔG° and E_a in kcal/mol, ΔS° in cal/(mol K). Error estimates: ΔH° , ± 0.5 kcal/mol; ΔS° , ± 1 cal/(mol K). ^d Error estimates for E_a , in kcal/mol: From standard deviation of slopes of Arrhenius plots for reaction 4r, ± 1.2 , and reaction 7r, ± 0.1 kcal/mol. Note that these E_a values are not exactly equal to the values derived from the two points given. For the other reactions, error estimates (kcal/mol) are based on $\pm 20\%$ in k in two-point temperature studies: 1r, ± 0.4 ; 2r, ± 0.4 ; 5r, ± 4.5 ; 8r, ± 2.5 ; 12r, ± 1.7 ; 15r, ± 1.3 .

$\exp(-\Delta G^\circ/RT)$. In cases where ΔG° is near 0, eqs 3 and 4 give a more general definition of fast kinetics.

According to eq 3, the sum of the efficiencies in the forward and reverse directions is near unity. In fact, the values for r_f and r_r in Table I range from 0.52 to 1.58, i.e. within 50% of unity. The scatter is expected from the estimated error in the rate constants. A similar relationship, $k_f + k_r < k_{\text{coll}}$ was noted in isotope exchange reactions.⁵

An exception is reaction 11 at 501 K, where $\Delta G^\circ = 0.2$ kcal/mol, and $r_f + r_r = 0.18$. This may be experimental error due to the low volatility of quinoline, or it may be an example of the known trend of fast type reactions to slow down by factors

of 2–10 near $\Delta G^\circ = 0$.¹ However, other reactions in Table I with small ΔG° do not show a slowing effect.

b. Relation to Thermochemistry. The reaction efficiency is determined uniquely by the equilibrium constant, i.e., by $K/(1+K)$, according to eq 4. The values of r and $K/(1+K)$ can be compared in Table I. The values agree within $\pm 50\%$ for most reactions. The scatter is consistent with $\pm 30\%$ error in k (and r), combined possibly with a similar error in K . An exception is again reaction 11 as noted above.

Entropy changes affect the kinetics through the effect on ΔG° and K according to relation 4. In reactions 1 and 2 the entropy changes are due to the rotational symmetries of the diatomic

neutral reactants and products. In reactions 3–5 the entropy effects are associated with conformational changes that result from the formation or dissociation of internal hydrogen bonds. We observed similar results in proton-transfer reactions involving polyfunctional amines and diketones, and in charge-transfer reactions involving alkanes. In both cases, the ions are constrained due to internal charge solvation.^{3,4}

In reaction 6 the entropy change is caused by rotational symmetry changes due to Jahn–Teller distortion of the $C_6H_6^+$ ion. In reactions 7–15, which involve anions, the entropy changes are due to the creation of an internal rotor in the transition $CH_3O^- \rightarrow CH_3OH$, and of overall molecular rotations in $OH^- \rightarrow H_2O$, $SH^- \rightarrow H_2S$ and $Cl^- \rightarrow HCl$. Evidently, entropy changes affect the kinetics regardless of their structural origin. Table I shows that the observed reaction efficiencies r are enhanced or decreased up to 3 orders of magnitude compared with the enthalpy factor $\exp(-\Delta H^\circ/RT)$. This is in agreement with eq 4 which reflects ΔG° , i.e. the overall thermochemistry. It is instructive to classify the reactions according to the various contributions to ΔG° .

i. Fast Exothermic Reactions. ($\Delta H^\circ < 0$, $\Delta G^\circ < 0$). In these reactions, both ΔH° and ΔG° are negative and the reaction efficiency assumes its largest possible value, which is unity (within experimental error). Some of these reactions do involve significant entropy changes, but since the kinetics are limited by nonthermodynamic factors, i.e. collision dynamics, the entropy changes have no kinetic effects. Examples are reactions 2f, 5f, 6f, and 9f in Table I. The large body of conventional fast exothermic reactions belongs in this class.

ii. Entropy-Enhanced Reactions. ($\Delta H^\circ > 0$, $\Delta G^\circ > 0$, $\Delta S^\circ > 0$). In the endergonic direction the reaction efficiency is smaller than unity. However, because of the positive entropy changes, the efficiency is not as small as it would be due to the enthalpy factor $\exp(-\Delta H^\circ/RT)$. For example, the positive entropy changes in reactions 5r, 6r, 9r, and 11f in Table I increase the reaction efficiencies by factors of 770–1035, 1.9, 41, and 3.2–5.9, respectively.

iii. Entropy-Driven Reactions. ($\Delta H^\circ > 0$, $\Delta G^\circ < 0$). These are special cases of entropy-enhanced reactions, in that $T\Delta S^\circ$ is large enough to reverse the sign between ΔH° and ΔG° . In accordance with eq 4, the reaction efficiency approaches unity. Examples are reactions 3f, 4f, 7f, 8f, 10f, and 12f–14f in Table I. Some show substantial entropy effects. For example, 3f and 4f would be slowed to efficiencies of 0.08 and 0.0012–0.028 by the enthalpy factor, but in fact the efficiencies are near unity.

iv. Entropy-Inhibited Reactions. ($\Delta H^\circ < 0$ or $\Delta H^\circ > 0$ and $\Delta G^\circ > 0$). Entropy effects can slow the reaction both in the exothermic and endothermic direction. In the exothermic case, these are the reverse of the entropy-driven processes in (iii). Although they are exothermic reactions, the efficiency is less than unity, because the large negative $T\Delta S^\circ$ term makes the reactions endergonic. The slow kinetics is in agreement with eq 4. Examples are reactions 3r, 4r, 7r, 8r, and 10r–15r in Table I. The second type of entropy-inhibited reactions are endothermic reactions. In this case, the entropy effect further slows the reaction, beyond the effect of the enthalpy term of $\exp(-\Delta H^\circ/RT)$. An example is reaction 2r in Table I.

c. Temperature Dependence. The rate constants at any temperature are expressed by eq 4, rewritten as (5).

$$k = k_{\text{coll}}(K/(1 + K)) \quad (5)$$

We also note the relation between Arrhenius activation energies and thermochemistry that results from the derivative of $(\ln(k_f/k_r)) = \ln K$ vs $1/T$, eq 6.

$$E_{a,f} - E_{a,r} = \Delta H^\circ_f \quad (6)$$

Equation 6 is a mathematical identity resulting from the definition of the Arrhenius activation energy. In the present reactions it leads to a straightforward relation between E_a and ΔH° , as follows.

For significantly exergonic reactions, $K \gg 1$. Therefore $k = k_{\text{coll}}$ and $E_{a,r} = 0$, since ion–molecule collision rates have zero or small temperature coefficients.¹² This is observed experimentally

in reactions 4f, 5f, 7f, 8f, 14f, and 15f in Table I. With $E_{a,r} = 0$, eq 6 gives $E_{a,f} = \Delta H^\circ_f$. This shows that the temperature dependence is determined by the sign of ΔH° in the slow, endergonic direction. This may give positive Arrhenius activation energies (reaction 5r in Table I) or negative Arrhenius activation energies (reactions 4r, 7r, 8r, and 14r in Table I).

The temperature dependence is more complex for reactions that are not significantly exergonic. When K is near unity, both k_f and k_r are temperature dependent according to eq 4, as, for example, in reactions 1 and 2 in Table I.

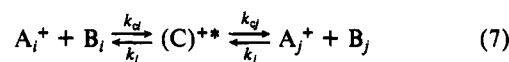
Because eq 5 is a mathematical identity, it must be exact. However, the experimental E_a and ΔH° values in Table I are similar but not identical. This is because E_a and ΔH° were derived from different sets of data. The E_a values were obtained from 2–8 temperature points, while ΔH° was calculated from larger sets of data.

The precision in a temperature study, conducted by using a constant mixture and pressure with only the temperature varied, is $\pm 20\%$ (the precision is better than the accuracy). In a limited temperature range, this may lead to a relatively large error in E_a (see Table I, footnote d). Within these limits, the E_a and ΔH° values agree.

The nature of the temperature dependence in “intrinsically fast” reactions of the present type is different from that in slow reactions. In slow reactions, the sign of the temperature coefficient depends on the central barrier,^{13–15} while in fast reactions it is determined by the overall thermochemistry.

2. General Formal Kinetics for Fast Reactions. The features of interest are the fast kinetics as in eq 3 and the relation to thermochemistry as in eq 4. As we saw, these relations are observed, within experimental accuracy, in the present reactions in Table I and also in previous measurements.^{3,4} Equations 3 and 4 were derived for reactions where the complex decomposes only in two channels, into “reactants” or “products”. However, fast reactions often have several channels such as competitive proton transfer, charge transfer, and H-atom and H_2 transfer. Lifshitz pointed out recently the need to generalize the formal kinetics for such cases.⁵

If every collision leads to products, i.e. if eq 1 or in the general case eq 3 applies, then evidently there occurs no reflection from barriers along the reaction path. This may be the case if there is a single reaction intermediate or if there are several rapidly interconverting intermediates. Indeed, the chemical transformations that occur indicate that there must be several interconverting intermediates. Nevertheless, the overall kinetic consequences of a single intermediate or several rapidly interconverting intermediates are equivalent in terms of the measurable overall rate parameters. Therefore the formal kinetics of fast reactions can be treated mathematically as involving a single common intermediate formed from the forward or reverse capture collisions. Correspondingly, in the scheme of eq 7, the intermediate $(C)^{+*}$



represents a single intermediate or several rapidly interconverting intermediates. The general scheme for reactions with n channels is written as eq 7.

The capture collision rate of A_i^+ with B_i is k_{ci} , and the unimolecular decomposition rate of the complex into channel i is k_i . The overall second-order rate constant leading from species $A_i^+ + B_i$ to $A_j^+ + B_j$ is given by k_{ij} in eq 8. The corresponding reaction efficiency is given by eq 9.

$$k_{ij} = k_{ci}k_j / \sum_i k_i \quad (8)$$

$$r_{ij} = k_j / \sum_i k_i \quad (9)$$

(12) Su, T.; Chesnavich, W. *J. Chem. Phys.* **1982**, *76*, 5813.

(13) Olmstead, W. N.; Brauman, J. I. *J. Am. Chem. Soc.* **1977**, *99*, 4219.

(14) Sharma, D. K.; Kebarle, P. *J. Am. Chem. Soc.* **1982**, *104*, 19.

(15) Stone, J. A. In *Structure, Reactivity and Thermochemistry of Ions*; Ausloos, P., Lias, S. G., Eds.; Reidel: Dordrecht, The Netherlands, 1987; p 391.

Note that the right side of eq 9 (and therefore also the left side) is independent of i . In other words, the efficiency of reaction into any product channel is the same regardless of which entrance channel (reactant pair) formed the complex, since once $(C)^{**}$ is formed through any channel, it decomposes statistically into all the channels. Therefore r_{ij} is independent of i , and can be denoted simply as r_j . Also note that $K_{i,i} = 1$ and $k_{i,i} = 0$.

The general relation between rate constants and equilibrium constants is given by eq 10.

$$K_{ij} = k_{ij}/k_{ji} = (k_{ci}/k_{cj})(k_j/k_i) \quad (10)$$

Equations 9 and 10 yield equation 11.

$$K_{ij} = (k_{ci}/k_{cj})(r_j/r_i) \cong r_j/r_i \quad (11)$$

The approximation in the last term of eq 11 is valid when the collision rate constants are similar, and in fact many ion-molecule collision rate constants are within 50% of $1.5 \times 10^{-9} \text{ cm}^3 \text{ s}^{-1}$. This simplifies the formulas below, which will be presented both with and without this approximation.

To compare with experiment, relationships between the measurable entities are needed. These are the equilibrium constants K_{ij} , the rate constants k_{ij} , and the efficiencies r_{ij} that may be calculated from the latter by using well-established equations for k_{ci} .¹² To relate these entities to each other, eq 8 can be inverted to obtain eq 12.

$$1/k_{ij} = (1/k_{ci})(\sum_i k_i/k_j) \quad (12)$$

Using eq 10 and inverting yields eq 13.

$$k_{ij} = k_{ci}/(\sum_i (k_{ci}/k_{cj})K_{j,i}) \cong k_{ci}/(\sum_i K_{j,i}) \quad (13)$$

Again, the approximation in the last term of eq 13 derives from equating all the collision rate constants. Remembering that $r_{ij} = r_j$ yields eq 14.

$$r_j = 1/\sum_i (k_{ci}/k_{cj})K_{j,i} \cong 1/\sum_i K_{j,i} \quad (14)$$

For $n = 2$, i.e., the simple two-channel case, noting that $K_{1,1} = 1$ and $K_{1,2} = 1/K_{2,1}$, eq 14 with the approximation reduces to eq 4.

Summing over j in eq 9 yields eq 15. This reduces to eq 3 for the simple two-channel case.

$$\sum_i r_i = 1 \quad (15)$$

Equations 14 and 15 apply to "intrinsically fast" reactions with n channels which may be exergonic or endergonic, and with any combination of enthalpy and entropy changes.

3. Mechanism. The preceding kinetic equations require no mechanistic information except the use of scheme 7. In fact, since the kinetics are fully controlled by the thermochemistry, no information about the potential energy surfaces is available from the observed kinetics. Nevertheless, some insights may be gained from the results.

The relation $K_{ij} \cong k_j/k_i$ (from eq 10) shows that the rate of dissociation of $(C)^{**}$ into each channel is proportional to the equilibrium distributions of the respective products. Therefore the transition states for decomposition into each channel are similar to the respective separated products.⁴ This is reasonable in ion-molecule systems where the transition states for capture (and dissociation) correspond to well-separated reactants. Therefore rotations formed (or frozen) in the reaction are already active (or frozen) in the transition states. For example, in the reaction $\text{Cl}^- + \text{H}_2\text{C}(\text{CN})_2 \rightarrow \text{HC}(\text{CN})_2^- + \text{HCl}$, dissociation into the endothermic forward channel is facilitated by the high density of states in the transition state. This is due to the molecular rotations of HCl at the transition state, where the ion and molecule are separated sufficiently to allow free rotations of HCl. A detailed RRKM model supports this conclusion.⁹

The scheme in eq 7 assumes a common intermediate (or series of intermediates), that is formed at the collision rate from any of the reactant (or product) pairs. According to eqs 8–14, the common complex must decompose into the competitive channels with relative rates similar to the equilibrium distribution of the

respective products. However, there are numerous instances where the most exothermic (or exergonic) channel is not dominant; this happens for example in reactions where charge transfer competes with heavy-particle (H^+ , H , or H_2) transfer. These reactions are not consistent with scheme 7; i.e., the products cannot be formed through a common intermediate that is formed in each collision. In such cases, products that are overrepresented vs their equilibrium distribution may be produced through a direct mechanism, while products that are underrepresented may form through kinetic barriers. These channels can compete with reaction proceeding through a common complex, as we saw in proton transfer from carbonium ions to amines.^{16,17} Therefore, product distributions can yield mechanistic information even when the overall reaction proceeds at the collision rate.

Of course, fast endothermic reactions must be consistent with the conservation of energy. The requirement is that the majority of the reactants and/or collisions have sufficient internal and/or translational energy that can be converted into potential energy to yield the products. In fact, the fast endothermic reactions in Table I and in previous work^{3,4} typically involve high temperatures, and reactants with many degrees of freedom, where these conditions can be met. In addition, under the present high-pressure conditions some reaction complexes may live long enough to undergo collisions, which can also contribute the required energy. It would be of interest to investigate entropy-driven reactions under low-pressure ICR conditions, to further clarify the source of the required energy.

A question exists about "entropy-driven" reactions under single-collision conditions where the entropy is not defined.² Such reactions may still proceed, since the mechanism depends on densities of states. The "entropy-driven" reactions result from the preferred decomposition of the reaction complex through transition states with high potential energies but high densities of states vs transition states with lower potential energies but also lower densities of states. The same energy factors and densities of states exist also when long-lived statistical complexes are formed in individual collisions. Therefore, the endothermic channel can still be preferred, due to the probability factors, if the energy requirements are fulfilled by the collision energy. It would be interesting to test this by related beam experiments on some of the "entropy-driven" reactions in Table I.

Conclusions

The present results generalize the notion of fast reactions. The general relations concerning reaction efficiency and thermochemistry are given by eqs 3 and 4, and for the case of multiple reaction channels, by eqs 14 and 15. According to these relations, fast reactions are characterized by thermochemical control; i.e., the efficiencies are determined completely and uniquely by the reaction free energy change.

Of special interest are fast endothermic reactions. We observed reactions endothermic up to 7 kcal/mol that proceed near unit collision efficiency because of entropy effects.

Fast endothermic reactions may be important at high temperatures. For example, many bimolecular exchange reactions involve entropy changes of 2–5 cal/(mol K). The present results suggest that under flame conditions at 1500–2000 K, reactions with such entropy changes may proceed at the capture collision rate even when endothermic by 4–10 kcal/mol. We note, however, that while these reactions may reach the capture rate, that rate itself may decrease at high temperatures by an order of magnitude due to entropy barriers.¹⁸ The study of ion-molecule kinetics at high temperatures will be of interest.

An analogy exists between entropy effects in fast and in slow ion-molecule reactions. The observed entropy-inhibited exothermic reactions (the reverse of entropy-driven reactions, see

(16) Meot-Ner (Mautner), M.; Field, F. H. *J. Am. Chem. Soc.* **1978**, *100*, 1356; **1979**, *101*, 2389.

(17) Meot-Ner (Mautner), M. In *Ion-Molecule Reactions*; Bowers, M. T., Ed.; Academic Press: New York, 1979; Vol. 1, p 198.

(18) Meot-Ner (Mautner), M.; Smith, S. C. *J. Am. Chem. Soc.* **1991**, *113*, 862.

above) are slowed because of the low density of states in the exit channel. This is analogous to the role of the low density of states at the central barrier in the double-well model for slow reactions.¹³ However, the properties of the central barrier can be deduced only indirectly, while the properties of the product-like transition states in the present reactions are known from the thermochemistry. In this sense, the present results give direct support for the postulated entropy effects in the double-well model.

The present work and other recent results^{18,19} extend the treatment of ion-molecule reactions to energy surfaces with

varying complexity. In the present model, fast reactions are accounted for by a single-well model. Slow reactions are described by a double-well model.¹³ Some slow reactions in hindered systems proceed through more complex surfaces with several free energy barriers and wells.^{18,19} In all the models, entropy (or density-of-states) factors at the barriers play significant roles.

Acknowledgment. I thank Dr. W. Tsang and Dr. L. W. Sieck for helpful discussions, and Dr. C. Lifshitz for suggesting the work on multichannel reactions. This work was supported in part by a grant from the Division of Chemical Sciences, Office of Basic Energy Sciences, U.S. Department of Energy.

(19) Sunner, J. A.; Hirao, K.; Kebabian, P. *J. Phys. Chem.* **1989**, *93*, 4010.

Electronic Quenching of CH(A²Δ), NH(A³Π), NH(c¹Π), and PH(A³Π) between 240 and 420 K

R. D. Kenner,[†] S. Pfannenberger,[‡] P. Heinrich, and F. Stuhl*

Physikalische Chemie I, Ruhr-Universität Bochum, D-4630 Bochum, Federal Republic of Germany
(Received: February 22, 1991; In Final Form: May 30, 1991)

Rate constants for electronic quenching of thermally equilibrated populations of CH(A), NH(A), NH(c), and PH(A) in $v = 0$ by nine collision partners between 240 and 420 K have been measured. These data have been augmented by using literature values of electronic quenching rate constants for these and other diatomic hydrides. This body of data is then used to examine the general applicability of the various classical models and methods used by previous authors in individual cases.

Introduction

The first- and second-row diatomic hydrides form a family of radical species that are important in a number of practical situations, i.e., combustion and air chemistry.^{1,2} They are also relatively simple species for which detailed quantum mechanical calculations can be performed.^{3,4} The rates of quenching of the electronically excited states of these species are often of interest in monitoring their concentrations by using laser-induced fluorescence.⁵ This paper presents the results of a study of the rates of collisional electronic quenching of several members of that family over the temperature range 240–420 K.

To get an overview of the temperature dependence of the quenching rates of electronically excited diatomic hydrides, a group of "standard" collision partners with a variety of properties was chosen. That group consists of three nonpolar diatomics (H₂, N₂, and O₂), one nonpolar triatomic (CO₂), two weakly polar molecules (CO and N₂O), two highly polar molecules (NH₃ and H₂O), and one representative alkane (C₂H₆). A few measurements were also made with C₂H₄ and some other hydrocarbons.

A number of different hydrides can be generated in the 193-nm laser photolysis: CH(A²Δ), NH(A³Π), NH(c¹Π), and PH(A³Π) were chosen for this study. To achieve immediate rotational and translational equilibrium, the experiments were performed in a very large excess of Ar. In addition to these species, OH(A²Σ⁺) is also conveniently generated, but some data are already available for quenching of that species between 200 and 400 K.^{6–8} Some data are also available for the rates of quenching of CH(A), NH(A), and OH(A) at temperatures greater than 900 K^{9–15} and BH(A¹Π),¹⁶ SiH(A²Δ),¹⁷ and SD(A²Σ)¹⁸ at room temperature.

Some of the data in the current work have been presented previously.¹⁹

Experimental Section

Apparatus. The electronically excited states of the hydrides investigated were generated by photolysis of appropriate parent

- (1) *Combustion Chemistry*; Gardiner Jr., W. C., Ed.; Springer: Berlin, 1984.
- (2) *Atmosphärische Spurenstoffe und ihr physikalisch-chemisches Verhalten*; Becker, K. H.; Löbel, J., Eds.; Springer: Berlin, 1985.
- (3) (a) Vegiri, A.; Farantos, S. C.; Papagiannakopoulos, P.; Fotakis, C. In *Selectivity in Chemical Reactions*; Whitehead, J. C., Ed.; Kluwer: Dordrecht, 1988; NATO AS, Ser. C 245, p 393. (b) Vegiri, A.; Farantos, S. C. *Mol. Phys.* **1990**, *69*, 129.
- (4) Jonas, R.; Staemmler, V. *Z. Phys. D* **1989**, *14*, 143.
- (5) Copeland, R. A.; Wise, M. L.; Rensberger, K. J.; Crosley, D. R. *Appl. Opt.* **1988**, *27*, 3679.
- (6) Copeland, R. A.; Crosley, D. R. *J. Chem. Phys.* **1986**, *84*, 3099.
- (7) Jefferies, J. B.; Copeland, R. A.; Crosley, D. R. *J. Chem. Phys.* **1986**, *85*, 1898.
- (8) Kenner, R. D.; Capetanakis, F. P.; Stuhl, F. *J. Phys. Chem.* **1990**, *94*, 2441.
- (9) Garland, N. L.; Crosley, D. R. *Chem. Phys. Lett.* **1987**, *134*, 189.
- (10) Crosley, D. R.; Rensberger, K. J.; Copeland, R. A. In *Selectivity in Chemical Reactions*; Whitehead, J. C., Ed.; Kluwer: Dordrecht, 1988; NATO AS, Ser. C 245, p 543.
- (11) Garland, N. L.; Crosley, D. R. *21st Symp. Int. Combust.* **1986**, 1693.
- (12) Garland, N. L.; Jefferies, J. B.; Crosley, D. R.; Smith, G. P.; Copeland, R. A. *J. Chem. Phys.* **1986**, *84*, 4970.
- (13) Rensberger, K. J.; Copeland, R. A.; Wise, M. L.; Crosley, D. R. *22nd Symp. Int. Combust.* **1988**, 1867.
- (14) Fairchild, P. W.; Smith, G. P.; Crosley, D. R. *J. Chem. Phys.* **1983**, *79*, 1795.
- (15) Smith, G. P.; Crosley, D. R. *J. Chem. Phys.* **1986**, *85*, 3896.
- (16) Douglass, C. H.; Rice, J. K. *J. Phys. Chem.* **1989**, *93*, 7659.
- (17) Nemoto, M.; Suzuki, A.; Nakamura, H.; Shibuya, K.; Obi, K. *Chem. Phys. Lett.* **1989**, *162*, 467.
- (18) Tice, J. J.; Ferris, M. J.; Wampler, F. B. *J. Chem. Phys.* **1983**, *79*, 130.
- (19) (a) Vlahoyannis, Y. P.; Hontzopoulos, E.; Vegiri, A.; Farantos, S. C.; Fotakis, C.; Browarzik, R. K.; Heinrich, P.; Kenner, R. D.; Rohrer, F.; Stuhl, F. *10th Int. Symp. Gas Kinet.*, Swansea, Wales, 1988. (b) Kenner, R. D.; Pfannenberger, S.; Heinrich, P.; Stuhl, F. *19th Int. Conf. Photochem.*, University of Michigan, Ann Arbor, MI, 1990.

[†]Current address: CSIRO Division of Applied Physics, P.O. Box 218, Lindfield, N.S.W. 2070, Australia.

[‡]Current address: Inno-Tec GmbH & Co. KG, Universitätsstrasse 150, D-4630 Bochum, Federal Republic of Germany.