

Kinetics of Hydrogen Halides in Shock Waves. II. A New Measurement of the Hydrogen Dissociation Rate

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Citation: *J. Chem. Phys.* **47**, 54 (1967); doi: 10.1063/1.1711890

View online: <http://dx.doi.org/10.1063/1.1711890>

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of magnitude for the triplet and between one and two orders of magnitude for the singlet. Addition of (p_0p_1) and (d_0p_1) configurations would greatly improve this result although these configurations were found to affect the energy by only about 0.00001 hartree.

The expectation values of z^2 and x^2 show differences of about 1% between the one- and two-center results, the error in the singlet being somewhat larger. These expectation values generally seem to be given relatively poorly by energetically accurate single-center functions. Hayes¹⁰ has computed the quadrupole moment for the ground state of H_2 using a 57-term single-center func-

tion ($E = -1.17258$ hartrees at $R = 1.4$ bohrs) and found a difference of over 6% compared to the value given by Kolos and Wolniewicz.¹⁴ These results indicate that even very energetically accurate single-center wavefunctions simply do not give a good first-order density matrix and that the effort needed to correct this situation would be far too great to be of practical utility. Therefore it is concluded that large-scale single-center calculations on very small systems is not worth the effort since more accurate results can be obtained more simply by other means.

¹⁴ W. Kolos and L. Wolniewicz, *J. Chem. Phys.* **43**, 2429 (1965)

Kinetics of Hydrogen Halides in Shock Waves. II. A New Measurement of the Hydrogen Dissociation Rate

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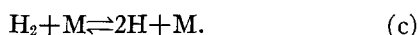
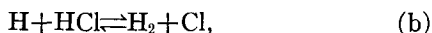
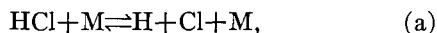
(Received 15 February 1967)

Decomposition rates for H_2 , diluted in Ar, were studied behind incident shock waves over the temperature range 2900° to 4700°K. HCl and the infrared emission from this molecule were used in a manner to trace the course of decomposition of the H_2 . In terms of recombination rate constants, we found (cc, moles, sec units) $k_{-3} = 10^{18} T^{-1}$, $k_{-4} = 2.5 k_{-3}$, and $k_{-5} = 20 k_{-3}$, where the subscripts 3, 4, and 5 refer respectively to Ar, H_2 , and H as third bodies.

I. INTRODUCTION

In our study of the kinetics of hydrogen halides in shock waves^{1,2} we have found it possible to gain a new measurement of the dissociation rate of H_2 . In particular we have used HCl, and the infrared emission from this molecule, in a manner to trace the course of decomposition of H_2 upon passage of a shock wave.

We describe and justify our procedures in detail below. Here we very briefly indicate our technique of measurement. In abbreviated form, the reaction scheme involved was as follows:



Reaction (b), it turned out, was very nearly in equilibrium under conditions of the study. Therefore, time-resolved measurements of HCl concentrations, along with mass balance and the equilibrium constant for Reaction (b), sufficed to determine H_2 -concentration histories. Experimentally, we observed emission from mixtures of nominally 5% H_2 , 1% HCl and 10% H_2 , 1% HCl (balance Ar). The arrangement of apparatus was identical to that described in our earlier papers.^{1,2}

¹ T. A. Jacobs, R. R. Giedt, and N. Cohen, *J. Chem. Phys.* **43**, 3688 (1965).

² T. A. Jacobs, N. Cohen, and R. R. Giedt, *J. Chem. Phys.* **6**, 1958 (1965).

Again, a digital computer was used in the analysis of the complete reaction scheme and to allow for the rather large drop in temperature brought about by the dissociation of substantial amounts of H_2 .

II. DATA ANALYSIS

Our experimental technique consisted first of recording the infrared-emission profiles from HCl, shock heated in mixtures of H_2 , HCl, and Ar. These records yielded plots of $(HCl)/(HCl)_0$ vs time where the subscript 0, here and elsewhere, refers to conditions immediately behind the shock. HCl was assumed to relax vibrationally within the time-resolution element of the experiment (1–2 μ sec); thus the observed infrared emission was assumed to characterize the molecule with internal modes fully equilibrated. Below we present emission data which support this assumption. Moreover, Borrell and Gutteridge³ have studied HCl relaxation in a shock tube to about 2300°K; extrapolation of their data to the range of the present work shows the relaxation of HCl to be less than 2 μ sec at the lowest temperature of our study.

Emissivity and blackbody corrections, compensating for the temperature decrease in the reaction zone, were applied in converting emission profiles to concentration profiles. In the present work, temperature drops were so

³ P. Borrell and R. Gutteridge, Vibrational Relaxation of HCl, AGARD, 38th Propulsion and Energetics Panel Meeting, Oslo, May 1966 (unpublished).

TABLE I. Reaction system.^a (Rate constants are in cc, moles, sec units, T is temperature, and R is the gas constant, here and throughout this paper.)

No.	Reaction	Rate constant	Ref.
1	$\text{HCl} + \text{M} \rightleftharpoons \text{H} + \text{Cl} + \text{M}$	$k_1 = 10^{21.83} T^{-2} \exp(-102\,170/RT)$	b
2	$\text{H} + \text{HCl} \rightleftharpoons \text{H}_2 + \text{Cl}$	$k_{-2} = 10^{13.92} \exp(-5480/RT)$	c, d
3	$\text{H}_2 + \text{Ar} \rightleftharpoons 2\text{H} + \text{Ar}$	$k_{-3} = 10^{18.0} T^{-1}$	This work
4	$\text{H}_2 + \text{H}_2 \rightleftharpoons 2\text{H} + \text{H}_2$	$k_{-4} = 2.5 k_{-3}$	This work
5	$\text{H}_2 + \text{H} \rightleftharpoons 2\text{H} + \text{H}$	$k_{-5} = 20 k_{-3}$	This work
6	$\text{HCl} + \text{Cl} \rightleftharpoons \text{H} + \text{Cl}_2$	$k_{-6} = [10^{9.7} \exp(1800/RT)] k_2$	e, f
7	$\text{Cl}_2 + \text{M} \rightleftharpoons 2\text{Cl} + \text{M}$	$k_7 = 10^{21.8} T^{-2.087} \exp(-57\,080/RT)$	g

^a $\text{M} = \text{Ar} + \text{HCl} + \text{H} + \text{Cl} + \text{H}_2 + \text{Cl}_2$. Reverse rates, in each case above, were computed from *JANAF Thermochemical Tables*, D. R. Stull, Ed. (The Dow Chemical Co., Midland, Mich. 1964).

^b Reference 2.

^c G. C. Fettes and J. H. Knox, *Progr. Reaction Kinetics* **2**, 22 (1964).

^d P. G. Ashmore and J. Chanmugam, *Trans. Faraday Soc.* **49**, 254 (1953).

^e R. L. Wilkins, Aerospace Corp. Rept. No. TDR-169(3230-10)TN-4, 1963; *J. Chem. Phys.* **42**, 806 (1965).

^f F. S. Klein and M. Wolfsberg, *J. Chem. Phys.* **34**, 1494 (1961).

^g T. A. Jacobs and R. R. Giedt, *J. Chem. Phys.* **39**, 749 (1963).

large (of order 1000°K) that some HCl always remained when the reaction mixture came to equilibrium; thus each experimental record yielded two independent measurements of the emissive properties of the heated HCl. Figure 1 presents these measurements as well as the temperature dependence we deduced for the gas emission. Points obtained in our earlier study of HCl alone are shown for comparison. The general agreement of data shown in Fig. 1 demonstrates the absence of any gross errors in application of emission techniques to a reaction zone of large temperature change. A word about the scatter of points (maximum of 10%, average of 3%) in Fig. 1 is in order. In general the scatter represents, in an absolute sense, errors incurred from run to run; these include errors in extrapolation, concentrations, initial pressures, and shock velocities, along with variations in detector and electronic stability and so forth. The subjective procedure of extrapolating experimental traces to the instant of shock arrival to determine frozen concentrations of HCl could be done

within an error of 1% to 2%; this was determined by study of computed time histories.

Our next step in analyzing data was to convert profiles of $(\text{HCl})/(\text{HCl})_0$ to profiles in $(\text{H}_2)/(\text{H}_2)_0$. We wish to present some evidence to justify our procedures in making this conversion. Table I shows the reaction scheme as included in the computer program. Table II shows computed results for a typical case, at a point where about 20% of the H_2 has dissociated. L is the rate of a reaction in Table I, the subscript denotes which reaction, and the plus and minus signs in subscripts refer to forward and reverse reactions. From the table we see that Reactions 6 and 7 play no role. Also it is seen that the forward and reverse rates of Reaction 2 are within about 0.3% of being equal; we found this equilibrium condition always to be established within 1% at about $1\ \mu\text{sec}$ behind the shock wave and to ap-

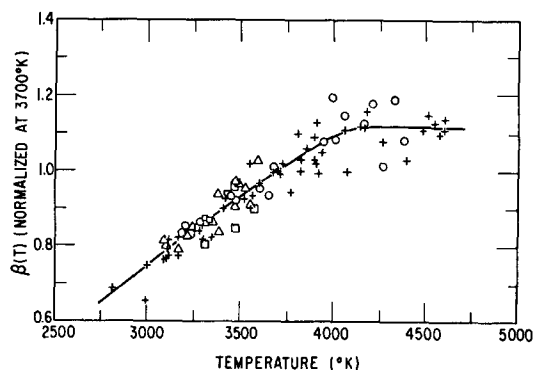


Fig. 1. Temperature variation of infrared emission from HCl. The parameter $\beta(T)$ measures the gas emission as recorded by a particular detection system; it is defined precisely in Ref. 2. —+— from Ref. 2; \odot 1% HCl, 5% H_2 , immediately behind shock wave; Δ 1% HCl, 5% H_2 , at equilibrium; \square 1% HCl, 10% H_2 , at equilibrium.

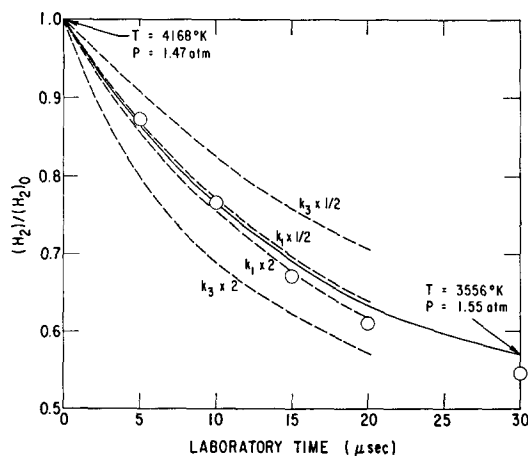


Fig. 2. Influence of rate constants on calculated concentration profiles. In the figure, we indicate the factor by which a particular rate constant is changed, all other rate constants remaining fixed as given in Table I. Run 615: 5% H_2 , 1% HCl, balance Ar; — rate constants from Table I; \odot experimental data.

TABLE II. Computed reaction rates (moles per cubic centimeter-second) for 5% H₂, 1% HCl in Ar at 0.785 fraction initial H₂ remaining ($T=3787^\circ\text{K}$ and $P=1.52$ atm).

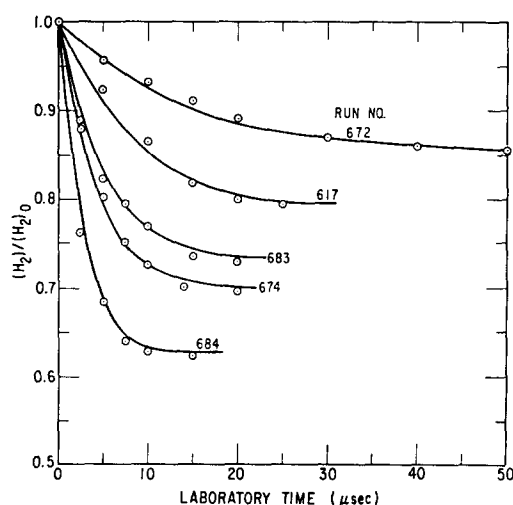
Reaction No.	L_i^a	L_{-i}^a
1	1.314 -4	1.728 -6
2	1.057 -1	1.054 -1
3	1.169 -3	1.540 -5
4	1.288 -4	1.698 -6
5	6.545 -4	8.626 -6
6	8.460 -5	8.251 -5
7	2.222 -6	2.995 -8

^a Numerals after first four figures indicate a power of 10; e.g., Reaction 1, $L_1=1.314 \times 10^{-4}$.

proach rapidly and remain below a few tenths of a percent throughout the run. Thus, Reaction 2 can be assumed to be in equilibrium for purposes of computing concentrations. It should be noted, however, that for the hydrogen rate, given by

$$-\partial(\text{H}_2)/\partial t = (L_3 - L_{-3}) + (L_4 - L_{-4}) + (L_5 - L_{-5}) - (L_2 - L_{-2}), \quad (1)$$

Reaction 2 [represented by the last term in Eq. (1)] still contributes about 17%. In Eq. (1) t is gas particle time and partial derivative refers to constant density ρ .



RUN NO.	TEMP. ($^\circ\text{K}$)		PRESS. (atm)		% H ₂	% HCl
	INITIAL	FINAL	INITIAL	FINAL		
672	3869	3225	1.41	1.49	10.52	I
617	4111	3331	1.50	1.60	10.45	I
683	4347	3431	1.60	1.71	10.48	I
674	4470	3481	1.65	1.77	10.52	I
684	4701	3581	1.76	1.89	10.46	I

FIG. 3. Theoretical and experimental concentration profiles. In the figure, initial temperature and pressure refer to values immediately behind the shock wave; final temperature and pressure refer to values at equilibrium. Composition for each run is shown also. \odot experimental data; — calculated.

With Reaction 2 taken to be in equilibrium, use of mass-balance relations gives

$$\frac{(\text{H}_2)}{(\text{H}_2)_0} = \frac{2 + [(\text{HCl})_0/(\text{H}_2)_0] \{1 - [(\text{HCl})/(\text{HCl})_0](\rho_0/\rho)\}}{(2\rho_0/\rho) + (1/K) \{[(\text{HCl})_0/(\text{HCl})] - (\rho_0/\rho)\}}, \quad (2)$$

with the equilibrium constant K given by

$$K = (\text{H}_2)(\text{Cl})/(\text{H})(\text{HCl}).$$

This equation was used to convert HCl profiles to H₂ profiles.

In using Eq. (2), we took the changing values of ρ_0/ρ and K in the region behind the shock wave from computer runs, performed using assumed values of the

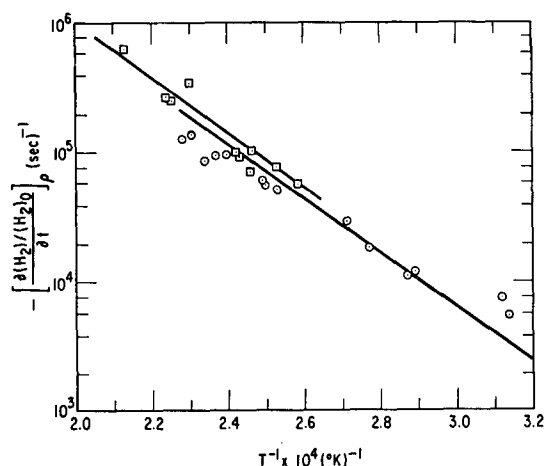


FIG. 4. Experimental and theoretically calculated initial slopes (at constant density) as a function of temperature. Total pressure for all runs is approximately 1.2 atm. \odot 5% H₂, 1% HCl, balance Ar; \square 10% H₂, 1% HCl, balance Ar; — calculated.

rate constants for H₂. An iterative procedure could have been employed with respect to these rate constants, by use of the experimental rate constants as they emerged in the analysis; however, our original estimates of the rates were sufficiently good that iteration was not required.

The final step in analyzing the data consisted of matching computed versions of hydrogen profiles with experimental observations. Rate constants for Reactions 3, 4, and 5 of Table I were varied in the matching procedure. Also, initial slopes of the experimental hydrogen profiles were compared with computed initial slopes.

An indication of error incurred in the profile-matching procedures can be gained by examination of Fig. 2. Here we show experimental and computed profiles for a 5% H₂, 1% HCl mixture. Also shown are the effects of varying, separately, k_1 and k_3 by factors of 2 and $\frac{1}{2}$, in each case with all other rate constants held fixed.

It can be seen that the profiles are quite sensitive to variations in the H_2 rate but quite insensitive to the HCl rate. These sensitivities are even more pronounced for mixtures containing 10% H_2 . On the other hand, the profiles were not very sensitive to variations in k_4

since this rate constant was found to contribute no more than about 25% to the net rate of H_2 dissociation. As H_2 dissociates, H atoms begin to contribute significantly to the net rate and the profiles begin to show sensitivity to choice of the k_5 rate constant; this can be seen in Table II where at only 15% H_2 dissociated, Reaction 5 contributes almost equally with Reaction 3. From such study, we estimated our error in measured rate constants at about a factor of 2.

III. DISCUSSION

The dissociation of H_2 diluted in Ar was observed over the temperature range 2900° to 4700°K. The values of k_{-3} , k_{-4} , and k_{-5} listed in Table I were found to yield a good match between experimental and computed concentration profiles and constitute the results of our experimental study. Analytic expressions for the dissociation rate constants can be derived by use of *JANAF* equilibrium data; we found

$$k_3 = 10^{18.62} T^{-1.025} \exp(-103\,240/RT)$$

with k_4 and k_5 given by the same expression multiplied by the appropriate efficiency listed in Table I. In Fig. 3 we show, for a selected number of runs with 10% mixtures of H_2 , the agreement achieved in matching concentration profiles. Initial slopes were taken from experimental profiles, and these are compared with theoretically calculated initial slopes in Fig. 4.

In Fig. 5 we compare rate constants derived in the present study with the work of other investigators. In the figures we present a summary of experimental rate data, given in terms of hydrogen recombination rate constants with Ar, H_2 , and H , respectively, as third bodies.

With the addition of the present work to the list of measurements, it appears that rate constants for H_2 dissociation, with Ar and H_2 as collision partners, are beginning to settle down to values acceptable within a factor of 2. On the other hand, reported dissociation rates with H as a collision partner scatter over an order of magnitude. Our measurements in this case (with what surely must look like the wisdom of hindsight) lie in the middle of the range of reported values.

It seems clear to us that future studies of the hydrogen system should concentrate on measurements of dissociation rates with the H atom as the collision partner.

ACKNOWLEDGMENTS

We must acknowledge that, essentially, the present experimental concept was suggested to us a few years ago by S. W. Benson. H. L. Williams ably assisted in performing the experiments; Mrs. B. Peer assisted with the manuscript; and Mrs. Karen Weld assisted with reduction of data. We again wish to acknowledge the U.S. Air Force for generous support, under Contract No. AF 04(695)-1001.

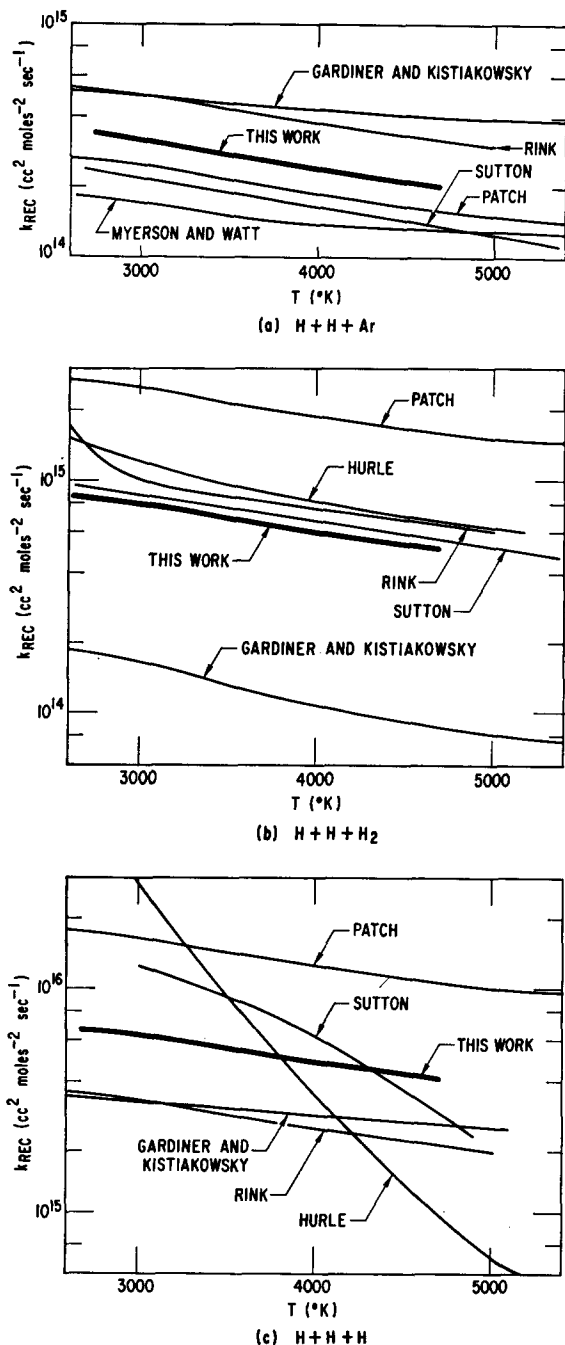


FIG. 5. Summary of experimental rate data for H_2 , given in terms of recombination rate constants. References for this figure: W. C. Gardiner and G. B. Kistiakowsky, *J. Chem. Phys.* **35**, 1765 (1961); I. R. Hurle, *Symp. Combust.* 11th, Berkeley, Calif., 1966 (to be published); A. L. Myerson and W. S. Watt, presented at 151st Am. Chem. Soc. Meeting, Pittsburgh, Pa., 1966; R. W. Patch, *J. Chem. Phys.* **36**, 1919 (1962); J. P. Rink, *J. Chem. Phys.* **36**, 262 (1962); E. A. Sutton, *J. Chem. Phys.* **36**, 2923 (1962).