

acidity of the proton bound to the pyrrole nitrogen and the formation of dinuclear imidazolato complexes. Studies on the binding of  $\text{CH}_3\text{Hg}^{\text{II}}$  by histidyl residues of peptides and proteins are in progress.

**Acknowledgments.** This research was supported in part by the National Research Council of Canada and the Swiss National Science Foundation.

## Reference and Notes

- (1) R. J. Sundberg and R. B. Martin, *Chem. Rev.*, **74**, 471 (1974).
- (2) Complexes 1–3 have been isolated from aqueous solution, and their compositions and structural formulas have been established by elemental analysis and NMR and Raman spectroscopy.
- (3) G. Schwarzenbach and M. Schellenberg, *Helv. Chim. Acta*, **48**, 28 (1965). However, vibrational spectra of crystalline  $\text{CH}_3\text{HgIm}$  provide evidence for intermolecular bonding, presumably involving the free nitrogen atom.
- (4) (a)  $K_4$  was calculated from  $K_1$ ,  $K_2$ , and the  $\text{p}K_A$  of the pyrrole nitrogen of  $\text{HIm}$ . For the NMR experiments, a  $\text{p}K_A$  of 14.44 was used;<sup>4b</sup> in the pH titration experiments, a  $\text{p}K_A$  of 14.3 was used.<sup>4c</sup> (b) P. George, G. I. H. Hanania, D. H. Irvine, and I. Abu-Issa, *J. Chem. Soc.*, 5689 (1964). (c) G. Geier and I. Erni, unpublished results.
- (5) (a) For comparison, the  $\text{p}K_A$  of the imidazole complex of aquocobalamin is 10.25<sup>5b</sup> and that of the imidazole in  $(\text{NH}_3)_5\text{CoHIm}^{2+}$  is 10.02.<sup>5c</sup> (b) G. I. H. Hanania and D. H. Irvine, *J. Chem. Soc.*, 5694 (1964). (c) J. Harrowfield, V. Norris, and A. M. Sargeson, *J. Am. Chem. Soc.*, **98**, 7282 (1976).
- (6) This is expected to be a good assumption because of the pronounced preference of  $\text{CH}_3\text{Hg}^{\text{II}}$  for a coordination number of one.
- (7) M. T. Fairhurst and D. L. Rabenstein, *Inorg. Chem.*, **14**, 1413 (1975), and references cited therein.

Christopher A. Evans, Dallas L. Rabenstein\*

Department of Chemistry, University of Alberta  
Edmonton, Canada

Gerhard Geier,\* Isidor W. Erni

Laboratorium für Anorganische Chemie  
Eidgenössische Technische Hochschule  
8092 Zurich, Switzerland

Received June 17, 1977

## Direct Calculation of the Equilibrium Value of the Energy of Activation for Dissociation of $\text{H}_2$ by Ar and Evidence for the Important Contribution of Collisional Dissociation from Low Vibrational Quantum Numbers and High Rotational Quantum Numbers at Shock Tube Temperatures

Sir:

Although dissociation of diatomic molecules under high-temperature steady-state conditions has been studied for over 20 years, the detailed interpretation of the results is still controversial. Two particularly important unresolved questions are the following.<sup>1–3</sup> (i) Why is the Arrhenius energy of activation  $E_a$ , defined by

$$E_a = -R \frac{d \ln k_d(T)}{d(1/T)} \quad (1)$$

where  $k_d(T)$  is the observed steady-state dissociation rate coefficient, much less (6 or more  $\text{kcal mol}^{-1}$  for typical systems) than the bond dissociation energy  $D_0$ ? (ii) Does dissociation proceed only or primarily from the topmost vibrational level (ladder climbing) or do lower vibrational levels make important contributions? These questions are complicated because it is necessary to consider the competition of energy transfer and dissociation which may result in a highly nonequilibrium population of the highest energy levels during the steady-state reaction.<sup>1–4</sup> It has usually been assumed that, if all states could be kept at equilibrium, dissociation would proceed primarily from the topmost vibrational energy level

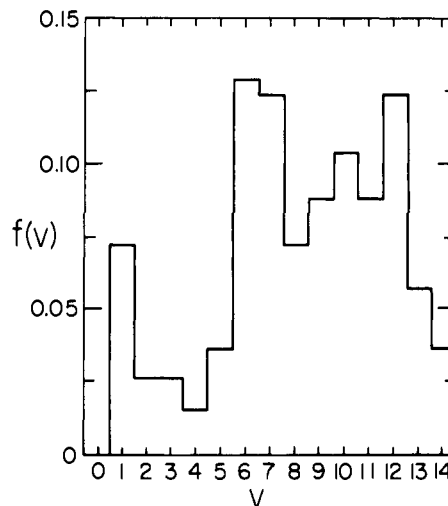


Figure 1. Calculated distribution of reactive collisions for the reaction  $\text{Ar} + \text{H}_2(v) \rightarrow \text{Ar} + \text{H} + \text{H}$  at local equilibrium of reactants at 4500 K sorted according to initial vibrational quantum number  $v$ .

and  $E_a$  would be significantly higher than observed. Attempts to understand the mechanism of the dissociation process have been hampered by the lack of accurate knowledge of the state-to-state transition rate coefficients.<sup>1–5</sup> Some workers<sup>6,7</sup> have used the classical trajectory method to study the dissociation process. Here we report a quasi-classical trajectory study<sup>8,9</sup> of the relative contribution to the dissociation rate of collisions with various initial vibrational quantum numbers  $v$  of para- $\text{H}_2$  dilute in Ar under conditions of local equilibrium of reactants<sup>10</sup> at 4500 K. We find large contributions from low  $v$ . Since vibrational nonequilibrium effects will tend to decrease the relative contribution of high- $v$  collisions, this implies even larger contributions from low- $v$  collisions for a rotationally equilibrated, vibrationally nonequilibrated steady state.<sup>11</sup> In addition we calculate that  $E_a$  at equilibrium is 6  $\text{kcal mol}^{-1}$  below  $D_0$ . Thus it is not necessary to invoke nonequilibrium effects solely because  $D_0$  considerably exceeds  $E_a$ .<sup>12</sup>

Our general methods and many other references are given elsewhere.<sup>9</sup> We used our own full potential surface,<sup>9</sup> which is the most accurate available. States of negative internal energy (compared with the separated-atom limit) are considered to be reactant states; quasi-bound  $\text{H}_2$  and dissociated  $\text{H}_2$  are considered to be product states.<sup>13</sup> We calculated 11 180 trajectories with maximum impact parameter 3.2 Å and with total energy in excess of the dissociation threshold but otherwise randomly sampled at 4500 K. We evaluated the equilibrium  $E_a$  by the Tolman definition,<sup>14</sup> i.e., at local equilibrium  $E_a$  is the average total energy of pairs that react minus that for all pairs. The result is  $E_a = 97.2 \pm 1.0 \text{ kcal mol}^{-1}$  (68% confidence limits). The critically evaluated 1972 recommended experimental value<sup>15</sup> (experiments involved normal  $\text{H}_2$ ) is  $96 \pm 4 \text{ kcal mol}^{-1}$  and a more recent experimental value<sup>16</sup> is 89  $\text{kcal mol}^{-1}$ . Since  $D_0$  is 103.3  $\text{kcal mol}^{-1}$ , a large negative deviation of  $E_a$  from  $D_0$  is predicted even under local equilibrium conditions. The local-equilibrium rate coefficient is calculated to be  $1.3 (\pm 0.1) \times 10^{-13} \text{ cm}^3 \text{ molecules}^{-1} \text{ s}^{-1}$  (68% confidence limits) compared with experimental values of  $15 \text{ } \left( \pm \frac{3}{2} \right) \times 10^{-15} \text{ cm}^3 \text{ molecules}^{-1} \text{ s}^{-1}$  and  $16 \text{ } 7.5 \times 10^{-15} \text{ cm}^3 \text{ molecules}^{-1} \text{ s}^{-1}$ . Thus the calculated local-equilibrium rate coefficient is larger than the observed rate coefficient. Nonequilibrium effects are expected<sup>1–3,6,17</sup> to decrease the rate.

Figure 1 shows the fraction  $f(v)$  of reacting trajectories with each initial  $v$ ; it shows 30% of the reaction comes from  $v = 1$ –6, 48% from  $v = 7$ –11, and only 22% from  $v = 12$ –14. For the typical  $v$ , the relative uncertainty in the histogram height due to the finite Monte Carlo sampling size is 28% (68% confi-

dence). Thus some of the structure in the figure may be statistical, but most of the reactive trajectories come from the highest bound ( $v, j$ ) states for each  $v$ , and so some of the maxima may be real; e.g., the large contributions from  $v = 1, 6, 7$ , and 12 are due to the particularly high reactivities of the (1,30), (6,22), (7,20), and (12,10) states, which are bound by just 0.52, 0.10, 0.61, and 0.02 kcal mol<sup>-1</sup>, respectively. The decrease of  $f(v)$  at high  $v$  is due to the low rotational partition functions for  $v \leq 13$ . These results show that the correct treatment of the equilibrium or nonequilibrium populations of low- $v$ , high- $j$  states as well as high vibrational levels is essential.<sup>18a,b</sup>

## References and Notes

- (1) H. Johnston and J. Birks, *Acc. Chem. Res.*, **5**, 327-335 (1972).
- (2) H. O. Pritchard In "Specialist Periodical Reports, Reaction Kinetics", Vol. 1, The Chemical Society, London, 1975, pp 243-290.
- (3) J. H. Kiefer, H. P. G. Joosten, and W. D. Breshears, *Chem. Phys. Lett.*, **30**, 424-428 (1975).
- (4) (a) J. E. Dove and D. G. Jones, *J. Chem. Phys.*, **55**, 1531 (1971); (b) J. E. Dove and D. G. Jones, *Chem. Phys. Lett.*, **17**, 134 (1972).
- (5) N. C. Blais and D. G. Truhlar in "State-to-State Chemistry", P. R. Brooks and E. F. Hayes, Ed., American Chemical Society, Washington, D.C., in press.
- (6) (a) V. H. Shui, J. P. Appleton, and J. C. Keck, *Int. Symp. Combust.*, **13th**, 1971, 21-35 (1971); (b) V. H. Shui and J. P. Appleton, *J. Chem. Phys.*, **55**, 3126-3132 (1971).
- (7) See also, e.g., (a) R. T. V. Kung and J. B. Anderson, *J. Chem. Phys.*, **60**, 3731-3743 (1974); (b) W. H. Wong and G. Burns, *Proc. R. Soc. London, Ser. A*, **341**, 105-119 (1974).
- (8) M. Karplus, R. N. Porter, and R. D. Sharma, *J. Chem. Phys.*, **43**, 3259-3287 (1965). Quasi-classical trajectories are classical except for the assignment of quantal values to initial vibrational and rotational action values so that the trajectories correspond to real ( $v, j$ ) states, where  $j$  is the initial rotational quantum number.
- (9) N. C. Blais and D. G. Truhlar, *J. Chem. Phys.*, **65**, 5335-5356 (1976).
- (10) This means that the ( $v, j$ ) states of H<sub>2</sub> and the relative translational motion are assumed to be in thermal equilibrium but the overall concentration of reactants is not in equilibrium with that of products. See R. K. Boyd, *Chem. Rev.*, **77**, 93-119 (1977).
- (11) See, e.g., ref 1. We find, however, that their assumed dissociation rate coefficients from selected initial low- $v$  levels are much too large compared with our calculated ones.
- (12) For similar conclusions see (a) H. O. Pritchard, *Can. J. Chem.*, **51**, 3152-3155 (1973); (b) H. O. Pritchard, *Acc. Chem. Res.*, **9**, 99-105 (1976); (c) G. W. Tregay, W. G. Valance, and D. I. McLean, *J. Chem. Phys.*, **59**, 1634-1640 (1973). However, we disagree with their treatments. References a and b assume that all quasi-bound states are reactant states in local equilibrium and that dissociation rate constants from initial states with selected  $j$  values have a simple dependence on centrifugal barrier height. Reference c assumes that the dissociation probability depends on  $v$  and translational energy but not on  $j$ .
- (13) This is essentially the same division into reactant and product states as used by R. E. Roberts, R. B. Bernstein, and C. F. Curtiss, *J. Chem. Phys.*, **50**, 5163-5176 (1969), to model the recombination of H atoms. We are presently studying the effect of considering the seven quasi-bound states with longest unimolecular lifetimes as reactant states.
- (14) (a) R. C. Tolman, "Statistical Mechanics with Applications to Physics and Chemistry", Chemical Catalog Co., New York, N.Y., 1927, pp 266-270; (b) R. H. Fowler and E. A. Guggenheim, "Statistical Mechanics", Macmillan, New York, N.Y., 1939, pp 489-504; (c) H. S. Johnston, "Gas Phase Reaction Rate Theory", Ronald Press, New York, N.Y., 1966, pp 215-217; (d) D. G. Truhlar, *J. Chem. Educ.*, in press, and references therein.
- (15) d. L. Baulch, D. D. Drysdale, D. G. Horne, and A. C. Lloyd, "Evaluated Kinetic Data for High Temperature Reactions", Vol. 1, CRC Press, Cleveland, Ohio, 1972, pp 309-323.
- (16) W. D. Breshears and P. F. Bird, *Int. Symp. Combust.*, **14th**, 1973, 211-217 (1973).
- (17) J. K. K. Ip and G. Burns, *J. Chem. Phys.*, **51**, 3425 (1969).
- (18) (a) This work was performed under the auspices of the U.S. Energy Research and Development Administration and was supported in part by the National Science Foundation under Grant No. CHE-7506416. (b) Portions of this work have been presented at the Second Joint Conference of the Chemical Institute of Canada and the American Chemical Society, Montreal, Canada, June 1, 1977. (c) Alfred P. Sloan Research Fellow, 1973-1977.

Donald G. Truhlar\*<sup>18c</sup>

Chemical Dynamics Laboratory  
Department of Chemistry, University of Minnesota  
Minneapolis, Minnesota 55455

Normand C. Blais\*

University of California  
Los Alamos Scientific Laboratory  
Los Alamos, New Mexico 87545

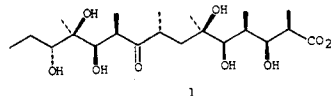
Received July 18, 1977

## Acyclic Stereoselection. 2.

### Synthesis of 3-Hydroxy-2-methyl- and 3-Hydroxy-2,4-dimethylcarboxylic Acids

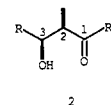
Sir:

One of the basic unsolved problems of organic synthesis is the stereoselective construction of acyclic compounds containing multiple chiral centers. This problem is best exemplified by the macrolide antibiotics as a whole and in particular by **1**, the open-chain form of the aglycone of the macrolide



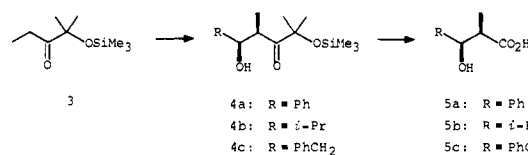
erythromycin A,<sup>1</sup> which has ten chiral centers. This polyhydroxy acid can be built up using a series of six aldol-type condensations, provided that sufficient control can be maintained over the stereochemical outcome of each condensation. This approach is similar to the biosynthesis of the macrolide aglycones in which the carbon skeleton is thought to originate from a series of condensations of acetyl- and propionyl-CoA units.<sup>2</sup>

We<sup>3</sup> and others<sup>4</sup> have previously reported examples of aldol condensations which afford  $\beta$ -hydroxy ketones **2** (R, R' = alkyl



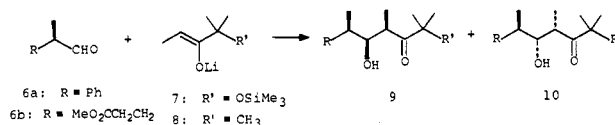
and/or aryl) in high diastereomeric purity.<sup>5</sup> We now report a simple modification which allows the production of  $\beta$ -hydroxycarboxylic acids **2** (R' = OH).

The enolate<sup>6</sup> of 2-methyl-2-trimethylsilyloxy-3-pentanone (**3**)<sup>7</sup> was condensed<sup>8</sup> with aldehydes to give  $\beta$ -hydroxy ketones (**4**) which were converted to  $\beta$ -hydroxy acids (**5**) upon treat-



ment with periodic acid. In each case, the relative stereochemistry about C-2 and C-3 has been assigned by consideration of the <sup>1</sup>H NMR coupling constant of the protons on these carbons.<sup>9</sup> We have not been able to detect any significant amounts of the other diastereomer in either the condensation or cleavage products (Table I). If the dianion of 2-hydroxy-2-methyl-3-pentanone is condensed with benzaldehyde, an 8:1 mixture of the two possible diastereomeric dihydroxy ketones is produced.

We have also examined the condensation of ketone enolates with aldehydes having a chiral center adjacent to the carbonyl group. For these condensations, there are four possible diastereomeric products,<sup>11</sup> but only **9** and **10** are detected. The



relative configuration about the first two centers is determined by the factors we have discussed previously.<sup>3</sup> The relative configuration about the second and third centers is that predicted by Cram's rule<sup>12</sup> (Table II).

To prove the stereostructures of the products **9** and **10** from these condensations, the hydroxy ketones from **6b** and **8** were converted to the lactones **11** and **12**. These lactones were separated by column chromatography and examination of their