# Isopiestic Study of the Complexes Diethyl Ether–Iodine and Hexane–Iodine in the Gas Phase

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**Abstract:** A sensitive microbalance technique has been employed to determine the effect of hexane and of diethyl ether vapors on the vapor-phase concentration of iodine in equilibrium with mixtures of the solid polyiodides $(CH_3)_4NI_5$ and $(CH_3)_4NI_9$. From these data, second virial cross coefficients and equilibrium constants for the formation of complexes of iodine with hexane and with diethyl ether have been inferred. Values of the formation constants for hexane–$I_2$ at 37° and diethyl ether–$I_2$ at 35° are 3.4 and 4.4 l. $mol^{-1}$, respectively. These results indicate that dispersion forces can play an important role in stabilizing weak molecular complexes. It is suggested that the gaseous adducts of aliphatic hydrocarbons with iodine—which have generally been regarded as contact-charge-transfer or collision complexes—differ little in stability or energy of complex formation from adducts of ethers or aromatic hydrocarbons with iodine.

The important effect of solvents on the energetics and spectra of molecular complexes has been noted by numerous investigators.[2-4] Recent studies indicate the need for accurate values of thermodynamic and spectral constants of gas-phase complexes, for which the complicating effects of solvent–solute interactions are absent.[3,5]

Although measurements of visible and ultraviolet spectra have been widely used to determine thermodynamic properties of charge-transfer (CT) complexes in condensed phases, spectral methods appear to be less generally applicable in studies of gas-phase complexes. Electronic spectra provide evidence for charge-transfer interaction in complexes such as benzene–$I_2$ and diethyl ether–$I_2$;[6] however, because of limitations in the accessible ranges of concentrations of vapors of the components, it is frequently difficult to resolve the product $K_c\epsilon$ (formation constant × extinction coefficient of the CT band) into separate values of $K_c$ and $\epsilon$.[5,7]

In order to supplement the information which can be obtained spectrally about electron donor–acceptor (EDA) interactions, we have begun a series of nonspectral (*viz.*, PVT, vapor density, isopiestic) studies of the formation of gas-phase complexes.[8] An important goal in these investigations is to learn more about the relative importance of specific interactions (*e.g.*, charge transfer and hydrogen bonding) and van der Waals forces in stabilizing gas-phase complexes. We report here results of a new gas-phase isopiestic technique which has been utilized to determine the equilibrium constant ($K_c$) for complexes of diethyl ether[8a] and of hexane with iodine. It has generally been assumed that charge-transfer forces account for a significant part of the stability of the ether–iodine complex,[6] whereas the hexane adduct is probably best described as a van der Waals complex, stabilized by nonspecific dispersion interactions.

## Experimental Technique

The gas-phase isopiestic method described here is analogous to isopiestic and solubility methods which have been applied previously in studying complex-formation equilibria in condensed phases.[4] It employs mixtures of solid tetramethylammonium pentaiodide ($TMAI_5$) and enneaiodide ($TMAI_9$) to maintain a constant activity of iodine in a gas-phase system. The equilibrium

$$TMAI_9(s) = TMAI_5(s) + 2I_2(g)$$

may be established in the presence and in the absence of controlled concentrations of a donor (D); increases in the vapor-phase concentration of iodine with increasing donor concentration are attributed to complex formation (*vide infra*).[8a,c]

The apparatus, which is sketched in Figure 1, consists of a fused silica microbalance, sealed inside a 3.4-l. all-glass, grease-free vacuum system fitted with two Teflon-bore stopcocks and submerged entirely in a constant-temperature water bath controlled to within 0.01°. The bucket (B), suspended from the balance arm, contains 40–100 mg of a mixture of $TMAI_5$ and $TMAI_9$.[9] In performing an experiment, the system is first evacuated through stopcock S; then, sufficient $I_2$ vapor is transferred into the system (from the $I_2$ reservoir, by opening stopcock R) to bring the balance pointer, P, to the desired rest point (as determined by reading the height of the pointer with a cathetometer). When the mass of solid has become constant (within about 2–4 hr if vapors other than $I_2$ have been removed from the system), donor vapors are transferred through stopcock S into the balance system by evaporation from a thermostated volumetric addition device (not shown). Equilibrium is reached within about 24 hr, as judged by observing the stabilization of the balance pointer at a new rest position.

In interpreting data, it is necessary to know accurately the activity of iodine in the gas phase ($a_{I_2}$) and the sensitivity of the microbalance. Previously reported values of the partial pressure of iodine in equilibrium with the solid polyiodide mixture were useful

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(1) (a) University of Oklahoma; (b) University of Oslo.

(2) (a) G. Briegleb, "Elektronen-Donator-Acceptor-Komplexe," Springer-Verlag, Berlin, 1961; (b) W. B. Person and R. S. Mulliken, "Molecular Complexes: A Lecture and Reprint Volume," Wiley, New York, N. Y., 1969.

(3) R. Foster, "Organic Charge-Transfer Complexes," Academic Press, New York, N. Y., 1969.

(4) S. D. Christian, A. A. Taha, and B. W. Gash, *Quart. Rev., Chem. Soc.*, **24**, 20 (1970).

(5) W. K. Duerksen and M. Tamres, *J. Amer. Chem. Soc.*, **90**, 1379 (1968); J. Grundnes and S. D. Christian, *ibid.*, 90, 2239 (1968), and references cited therein.

(6) (a) F. T. Lang and R. L. Strong, *ibid.*, 87, 2345 (1965); (b) J. Grundnes and M. Tamres, manuscript in preparation.

(7) W. B. Person, *J. Amer. Chem. Soc.*, 87, 167 (1965).

(8) (a) J. Grundnes, S. D. Christian, and V. Cheam, *Acta Chem. Scand.*, **24**, 1836 (1970); (b) S. D. Christian, E. E. Tucker, and H. E. Affsprung, *Spectrochim. Acta, Part A*, 23, 1185 (1967); (c) J. D. Childs, S. D. Christian, J. Grundnes, and S. R. Roach, *Acta Chem. Scand.*, in press; (d) J. Grundnes, S. D. Christian, V. Cheam, and S. B. Farnham, *J. Amer. Chem. Soc.*, **93**, 20 (1971).

(9) Before the balance is sealed in the system, the bucket is loaded with pure $TMAI_5$, prepared as described by F. D. Chattaway and G. Hoyle, *J. Chem. Soc.*, 123, 654 (1923). Less $TMAI_5$ is utilized than the amount required to tip the balance to a level position, since $I_2$ vapors can be allowed to react with the solid $TMAI_5$ after the balance is installed, thereby converting some of the compound to $TMAI_9$.

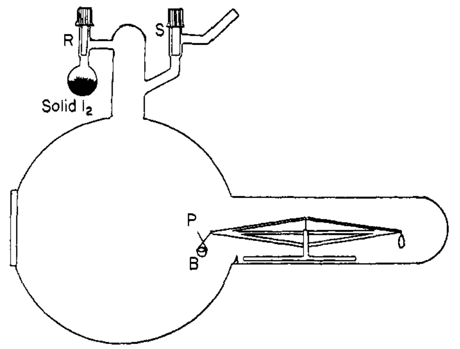

Figure 1. Vapor-phase isopiestic apparatus.

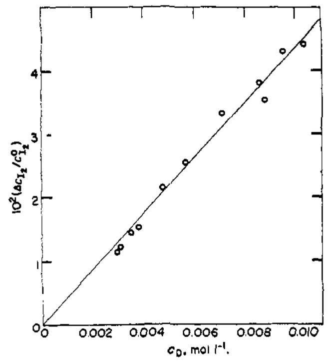

Figure 2. Increase in equilibrium concentration of iodine in the presence of diethyl ether vapors.

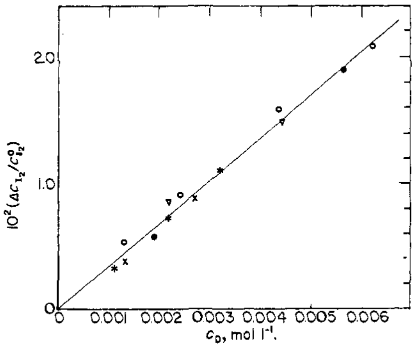

Figure 3. Increase in equilibrium concentration of iodine in the presence of hexane vapors: O, *, 37.3°; ∇, 37.2°; ×, 37.6°; ●, 36.7°.

in estimating $a_{I_2}$ at temperatures of interest;[8c] however, it was felt that values of the activity should be determined under conditions closely approximating those prevailing in the isopiestic experiments. The following bithermal equilibration experiment was performed to determine the partial pressure of iodine in the TMAI$_5$(s)-TMAI$_9$(s)-I$_2$(g) system. An auxiliary vacuum system, including an external reservoir of solid iodine, connecting tubing, and Teflon-bore stopcocks, was joined to the gas-phase isopiestic apparatus through stopcock S. Equilibrium was established in the balance system, thermostated at a temperature in the range 35–40° to ±0.01°, and the connecting tubes were evacuated; the external iodine reservoir was maintained at a temperature in the range 13.5–18.5°. With stopcock S open, observations were made of the displacement of the balance pointer—if the iodine reservoir was held at too high a temperature, the mass of the polyiodide sample increased, and if the reservoir temperature was too low, the mass decreased. By plotting the displacement of the pointer against time, it was possible to determine rates of transfer of iodine to or from the polyiodide sample as a function of temperature, and thereby to infer pairs of temperature values ($T_p$ and $T_{I_2}$, the temperatures of the polyiodide sample and solid iodine sample, respectively) corresponding to vapor equilibrium between the two samples. The reproducibility of these pairs of values was excellent; discrepancies between values of $T_{I_2}$ for a fixed $T_p$ did not exceed ±0.05° in successive experiments. The results obtained were: 40.00, 18.35°; 37.50, 16.07°; 35.00, 13.95° for equilibrium pairs of $T_p$, $T_{I_2}$ values. By utilizing these data and the accurate vapor pressure data for solid iodine reported by Gillespie and Fraser,[10] the values $p_{I_2} = 0.142 \pm 0.001$ Torr and $\Delta H = 15.2 \pm 0.3$ kcal were obtained for the reaction $0.5\mathrm{TMAI_9(s)} = 0.5\mathrm{TMAI_5(s)} + \mathrm{I_2(g)}$ at 37.50°.

Knowledge of $p_{I_2}$ in the range of temperatures employed in the isopiestic experiments permitted the development of an accurate method for calibrating the balance under conditions of use. By using the van't Hoff relation and values of $p_{I_2}$ and $\Delta H$ at 37.50°, it was possible to calculate $p_{I_2}$ and the molar concentration of I$_2$ at various temperatures at which the bath was thermostated. (It was assumed that I$_2$ vapors may be treated as ideal in the absence of added donor.) Thus, upon increasing the bath temperature by a known amount, it could be calculated that the number of moles of iodine in the solid mixture decreased by $V\Delta c_{I_2}$, where $\Delta c_{I_2}$ is the increase in the vapor concentration of iodine and $V$ is the system volume, known to within 0.5%. By measuring the change in pointer height corresponding to this change in temperature and sample mass, the balance sensitivity could be calculated. In the case of the balance used in the ether experiments, the sensitivity inferred from the dependence of pointer height on temperature agreed to within 2 or 3% with that determined by calibrating the balance outside the isopiestic apparatus with known weights (21.3 mm/mg at midscale). The balance used in the hexane experiments was considerably more sensitive (214 mm/mg at midscale); it was calibrated solely by measuring the effect of temperature on pointer level.

Adsorption effects did not appear to be important in isopiestic experiments with ether; however, with hexane, an initial weight increase of the sample in the bucket always occurred during the period of hexane addition (10–15 min). The maximum weight of the polyiodide mixture was attained within a few minutes after the hexane sample had been added. Since the subsequent loss of iodine from the solid took place gradually, during a period of at least several hours, it was not difficult to extrapolate back to an initial sample weight including adsorbed hexane. It appeared that further adsorption did not occur to a significant extent beyond 5 or 10 min after the addition of hexane. The initial half milliliter or so of hexane (liquid) added produced so large an adsorption effect that it was not possible to determine a reliable initial sample weight for the first increment. Therefore, the system was preequilibrated with at least 0.5–0.8 ml of hexane before accurate measurements were commenced. A buoyancy correction was required in the ether experiments, because the buoyant effect of vapors on the denser polyiodide sample is less than that on the compensating mass of silica at the opposite end of the balance. The magnitude of the correction for buoyancy amounted to about 7% of the total isopiestic effect with ether at 35°. In the hexane system, buoyancy effects were automatically accounted for along with adsorption in the extrapolation procedure used to obtain the corrected initial polyiodide sample weight. With hexane, the total correction equaled approximately 20% of the isopiestic effect. (This corresponds to about 5 or 10 $\mu$g for a typical pressure increment of 20–40 Torr.)

Attempts to study benzene-I$_2$ with the present technique were only marginally successful. An isopiestic effect comparable to that obtained with hexane was observed, but reproducibility of the measurements was poor. Presumably, continued adsorption and/or compound formation between benzene and the tetramethylammonium polyiodides occurred throughout time period in which the isopiestic effect was being measured.

## Results and Interpretation

Figures 2 and 3 are plots of $\Delta c_{I_2}/c_{I_2}^0$ (the increase in iodine concentration in the vapor phase divided by the initial concentration of iodine in the absence of donor) against $c_D$ (the total vapor concentration of diethyl ether and of hexane, respectively). Most of the points for the ether system represent data taken for single addi-

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[10] L. J. Gillespie and L. H. D. Fraser, *J. Amer. Chem. Soc.*, 58, 2260 (1936).

tions of ether to the preequilibrated system $TMAI_5(s)$–$TMAI_9(s)$–$I_2(g)$, although in a few instances the additivity of the effect was confirmed by making measurements on two or three samples of ether introduced successively without reevacuating the chamber. In the hexane experiments, advantage was taken of the greater sensitivity of the balance, in that smaller samples were added successively to the preequilibrated system $TMAI_5(s)$–$TMAI_9(s)$–$I_2$, hexane vapor; the cumulative effect of these additions for several series of samples is plotted in Figure 3.

The linearity of the plots makes it possible to determine limiting values of the function $(1/c_{I_2}{}^0)(\partial c_{I_2}/\partial c_D)_{a_{I_2}}$ for the two systems. This expression may be equated to $-2B_{12}$ (where $B_{12}$ is the second virial cross coefficient between iodine and the other vapor component), provided one makes the reasonable assumptions that the fugacity of the solid polyiodide mixture is not influenced by variations in total pressure in the range of pressures employed, that the ether and hexane vapors behave ideally, and that $c_D \gg c_{I_2}$.[11] Least-squares analysis of the data displayed in Figures 2 and 3 yields the values $B_{12} = -(2.18 \pm 0.04)$ and $-(1.68 \pm 0.04)$ l. mol$^{-1}$ for the diethyl ether–iodine and hexane–iodine systems, respectively.

Our interpretation of the values of $B_{12}$ is that they may be converted directly into equilibrium constants for formation of the 1:1 complex. Following Rice,[12] one may derive the relation

$$K_c = -2B_{12} + (4/3)N\pi r_{0,12}{}^3 \qquad (1)$$

where $r_{0,12}$ is approximately equal to the mean of the molecular radii of iodine and the organic species and $N$ is Avogadro's number. The last term in (1) is only on the order of 2 or 3% of the value of $K_c$, and considering the uncertainties in estimating $r_{0,12}$ for reasonable geometries of the complex, we have neglected the term in calculating $K_c$. We report the values $K_c = (4.35 \pm 0.30)$ l. mol$^{-1}$ at 35° and $(3.35 \pm 0.30)$ l. mol$^{-1}$ at 37° for the complexes diethyl ether–$I_2$ and hexane–$I_2$, respectively.[13]

It should be mentioned that the determination of $K_c$ from the gas-phase isopiestic results could have been accomplished more simply by attributing the increase in concentration of iodine in the gas phase, in the presence of donor, to formation of the complex; this is consistent with the procedure usually followed in inferring complex formation constants from isopiestic or solubility experiments on condensed phases.[4] Thus, $K_c = \Delta c_{I_2}/(c_D c_{I_2}{}^0)$, where $\Delta c_{I_2}$ is the increase in total iodine concentration at the donor concentration $c_D$. Values of $K_c$ entirely equivalent to those determined from $B_{12}$ are obtained in this way.

## Discussion

Thermodynamic constants have been obtained for diethyl ether–$I_2$ from spectral measurements; Lang and Strong report $K_c = 5.5$ l. mol$^{-1}$ (extrapolated to 35°) and $\Delta E = -2.6$ kcal mol$^{-1}$.[6b] An early report by Brüll[14] and Ellerbock presents transpiration measurements, from which it is possible to estimate the values $K_c = 6$ l. mol$^{-1}$ at 35° and $\Delta E = -3$ kcal mol$^{-1}$, using an analysis similar to that described in the preceding section. No estimates appear to have been made of the stability constant of 1:1 complexes between hexane and iodine; in fact, the CT spectra observed for four aliphatic hydrocarbon molecules interacting with iodine[15] did not permit a distinction to be made between so-called contact-charge-transfer complexes[16] and discrete molecular complexes with small but finite values of $K_c$. It may be considered surprising, therefore, that the $K_c$ value given here for hexane–$I_2$ (3.4 l. mol$^{-1}$ at 37°) is comparable to values which have been reported previously for benzene–$I_2$ (4.1 and 3.0 l. mol$^{-1}$, extrapolated to 37°).[6a,17]

The diethyl ether–$I_2$ complex formation constant obtained here agrees to within 20% with the value determined spectrally (extrapolated to 35°).[6a] Moreover, in spite of the uncertainty in the spectrally determined $K_c$ value, the reported values of $K_c\epsilon$[6] are probably reliable; thus, it is possible to calculate $\epsilon$ for the CT band by combining results of the present research with the spectral results. In this way, the values $\epsilon = 2700$ and 2450 l. mol$^{-1}$ cm$^{-1}$ are inferred. An important result of the present research is, therefore, that it confirms the previous conclusion that $\epsilon$ is considerably lower for the CT band of diethyl ether–$I_2$ in the vapor phase than in solution.[6a]

We believe the results for the hexane system provide clear evidence that van der Waals forces can play a significant role in stabilizing molecular complexes between organic molecules and iodine. Atack and Rice[17] have concluded that benzene–$I_2$ is primarily a van der Waals complex, which exhibits little preference for a particular molecular orientation, at least in the gas phase. The present results indicate that in the absence of interactions with solvent molecules the stability of hexane–$I_2$ approximates that of benzene–$I_2$ and nearly equals that of diethyl ether–$I_2$, in spite of the fact that specific charge-transfer interactions are presumably absent in hexane–$I_2$. Thus, one may question the desirability of applying the label "contact-charge-transfer complexes" to aliphatic hydrocarbon–iodine adducts. Equilibrium constants in the range reported here (3 to 5 l. mol$^{-1}$) are more than an order of magnitude larger than those estimated for collision complexes of iodine with aliphatic hydrocarbons;[15] moreover, the thermodynamic results provide no basis for making a qualitative distinction between aliphatic hydrocarbon–iodine adducts and complexes such as diethyl ether–$I_2$ and benzene–$I_2$.

A relative measure of the ability of a molecular species to interact with another through dispersion forces is given by values of the van der Waals $a$ and the molecular polarizability of that species. Table I lists values of these constants for several molecules of interest here, as well as $K_c$ and $-\Delta E$ for 1:1 molecular complexes of these molecules with iodine. Included in the table are constants for $CO_2$; the $K_c$ value for $CO_2$–$I_2$ has been estimated from measurements of the solubility of $I_2$ in gaseous $CO_2$. If dispersion forces alone operate to

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[11] M. Rigby and J. M. Prausnitz, *J. Phys. Chem.*, 72, 330 (1968).

[12] O. K. Rice, "Statistical Mechanics, Thermodynamics and Kinetics," W. H. Freeman, San Francisco, Calif., 1967.

[13] The larger relative error limits in $K_c$, compared to the least-squares errors in $B_{12}$ given above, reflect our estimates of the uncertainty in corrections for buoyancy and adsorption and balance calibration.

[14] W. Brüll and W. Ellerbrock, *Z. Anorg. Allg. Chem.*, **216**, 353 (1934).

[15] M. Tamres and J. Grundnes, *J. Amer. Chem. Soc.*, **93**, 801 (1971).

[16] L. E. Orgel and R. S. Mulliken, *ibid.*, **79**, 4839 (1957).

[17] D. Atack and O. K. Rice, *J. Phys. Chem.*, 58, 1017 (1954).

**Table I.** Values of van der Waals $a$ and Molecular Polarizability, $\alpha$, for Several Molecules and Thermodynamic Constants for Formation of Gas-Phase Complexes with $I_2$

| Compound | Temp, °C | $K_c$,[a] l. mol$^{-1}$ | $-\Delta E$,[a] kcal | Ref | $a$,[b] l.$^2$ atm mol$^{-1}$ | $\alpha \times 10^{25}$,[b] cm$^3$ |
|---|---|---|---|---|---|---|
| Hexane | 37 | 3.4 | | *c* | 24.8 | 117.8 |
| Benzene | 35 | 4.2 | 1.4 | *d* | 18.7 | 103.2 |
| | 35 | 3.1 | 1.8 | *e* | | |
| Diethyl ether | 35 | 4.4 | | *c* | 17.4 | 87.3 |
| | 35 | 5.5 | 2.6 | *d* | | |
| | 35 | | 4.0 | *f* | | |
| | 35 | 6 | 3 | *g* | | |
| Carbon dioxide | 35 | 0.8 | 1.4 | *h* | 3.6 | 26.5 |

[a] For formation of the 1:1 complex between compound and $I_2$; extrapolated to temperature indicated if necessary. [b] As tabulated in J. R Partington, "An Advanced Treatise on Physical Chemistry," Longmans, Green and Co., London, 1954; Landolt-Bornstein, "Zahlenwerte und Functionen," Vol. I, Part 3, Springer-Verlag, Berlin, 1951, pp 510–512. [c] This work. [d] F. T. Lang and R. L. Strong, *J. Amer. Chem. Soc.*, **87**, 2345 (1965). [e] D. Atack and O. K. Rice, *J. Phys. Chem.*, **58**, 1017 (1954). [f] J. Grundnes and M. Tamres, in press. [g] Calculated from gas solubility data of W. Brüll and W. Ellerbrock, *Z. Anorg. Allg. Chem.*, **216**, 353 (1934). [h] Calculated from gas-phase solubility data of H. Braune and F. Strassman, *Z. Phys. Chem., Abt. A*, **143**, 225 (1929).

stabilize the 1:1 complexes, the order of $K_c$ and $-\Delta E$ values should be hexane > benzene > diethyl ether > $CO_2$. Assuming that hexane–$I_2$ is stabilized solely by van der Waals forces, one may estimate that the stability of diethyl ether–$I_2$ owes roughly 50% to CT interaction and 50% to dispersion. The benzene–$I_2$ complex is probably stabilized less than 25% by CT forces. Although these conclusions are qualitative and tentative, they do lend support to recent arguments that values of $\epsilon$ for CT bands of gaseous complexes are lower than the corresponding condensed-phase values because of the variety of molecular arrangements which can contribute to the stability of the 1:1 complex.[18] Most of the molecular forms of weak gas-phase complexes presumably do not contribute significantly to the intensity of the CT band, whereas in the case of complexes in solution, the values determined for $K_c$ and $\epsilon$ may pertain more nearly to oriented CT complexes.[18, 19]

**Acknowledgment.** Financial aid from National Science Foundation under Grants No. GP-8029 and GP-23278 is greatly appreciated.

(18) O. K. Rice, *Int. J. Quantum Chem., Suppl.*, **2**, 219 (1968).

(19) However, there is still considerable discussion regarding the interpretation and validity of values of $K_c$ and $\epsilon$ for weak CT complexes in solution; see, for example, ref 2b and 3 and R. L. Scott and D. V. Fenby, *Annu. Rev. Phys. Chem.*, **20**, 125 (1969).

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# Reactions of Borane. II.[1] Absolute Rate of the Reaction of Borane with Ethylene in the Gas Phase

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**Abstract:** The reaction of borane ($BH_3$) with ethylene ($C_2H_4$) to produce ethylborane ($C_2H_5BH_2$) as a primary product has been shown to occur in the gas phase. At 450° and 4.7 Torr total pressure of helium, the absolute bimolecular rate constant for this reaction is given by the expression $\log k_1 = 10.2 - (2{,}000/4.575T)$ l. mol$^{-1}$ sec$^{-1}$. Estimates of the rate constants for the self-association and hydroboration of ethylborane are also presented. The significance of these results with respect to the reactivity of borane and the nature of the hydroboration reaction are discussed in terms of the absolute rate theory.

We have recently reported measurements on the rate of the self-association reaction of borane, $BH_3$, to form diborane, $B_2H_6$.[1] This reaction is one of the characteristic reactions of the borane molecule, and these measurements have illustrated one aspect of the reactivity of this unstable species. In an attempt to further our understanding of the reactivity of a species possessing a free valence orbital, we have now both qualitatively and quantitatively examined the reaction of free borane with ethylene. This reaction is the prototype of the hydroboration reaction—a reaction which has been studied extensively in the liquid phase and in solvent systems.[2] In these studies, it is diborane or a borane–solvent adduct and the olefin which are the initial reactants. A few gas-phase studies have been reported,[3–5] and here, too, diborane is the initial reactant. Of course this does not necessarily mean that the olefin reacts directly with either diborane or the borane–solvent adduct, as it is possible that free borane is an active intermediate. In order

(1) Part I: G. W. Mappes, S. A. Fridmann, and T. P. Fehlner, *J. Phys. Chem.*, **74**, 3307 (1970).

(2) H. C. Brown, "Hydroboration," W. A. Benjamin, New York, N. Y., 1962.

(3) D. T. Hurd, *J. Amer. Chem. Soc.*, **70**, 2053 (1948).

(4) A. T. Whatley and R. N. Pease, *ibid.*, **76**, 835 (1954).

(5) H. H. Lindner and T. Onak, *ibid.*, **88**, 1886 (1966).