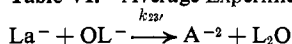


Table VI. Average Experimental Rate Constants in 0.1 M Ionic Strength Water and D₂O Solutions at 25° for the Reaction

Acid	$k_{23}^{\text{H}}, M^{-1} \text{sec.}^{-1} \text{ }^a$	$k_{23}^{\text{D}}, M^{-1} \text{sec.}^{-1} \text{ }^b$	$k^{\text{H}}/k^{\text{D}}$
<i>cis</i> -Caronic	$(6.33 \pm 0.77)10^7$	$(5.85 \pm 0.72)10^7$	1.1
<i>cis</i> -3,3-Diphenylcyclopropane-1,2-dicarboxylic	$(4.43 \pm 1.17)10^8$	$(2.79 \pm 0.70)10^8$	1.6
Tetramethylsuccinic	$(2.54 \pm 0.25)10^8$	$(2.40 \pm 0.21)10^8$	1.1
Tetraethylsuccinic	$(5.31 \pm 0.85)10^7$	$(4.43 \pm 0.97)10^7$	1.2
<i>rac</i> - α, α' -Di- <i>t</i> -butylsuccinic	$(2.29 \pm 0.53)10^8$	$(1.36 \pm 0.17)10^8$	1.7

^a Average rate constant calculated from eq. 7 for data in water. ^b Average rate constant calculated from eq. 7 for data in D₂O.

could yield a primary kinetic isotope effect as large as 6 or 8.²⁰ Since the experimental effect is a product of primary and secondary solvent kinetic isotope effects, it is interesting to estimate the secondary solvent kinetic isotope effect from stretching frequencies suggested by Bunton and Shiner²¹ and Bigeleisen's equation

$$(k^{\text{H}}/k^{\text{D}})_{\text{sec}} = \text{antilog} \frac{\sum \nu^{\text{H}} - \sum \nu^{\text{H}*}}{12.53T} \quad (8)$$

derived from absolute rate theory. Postulating a monoanion that lacks an intramolecular hydrogen bond but has six hydrogen bonds to solvent and an activated complex having a variety of possible structures, we calculate values of a secondary $k^{\text{H}}/k^{\text{D}}$ in the

(20) C. G. Swain, D. A. Kuhn, and R. L. Schowen, *J. Am. Chem. Soc.*, **87**, 1553 (1965).

(21) C. A. Bunton and V. J. Shiner, Jr., *ibid.*, **83**, 42, 3207, 3214 (1961).

range 0.2 to 0.6.²² Even the introduction of an intramolecular hydrogen bond in the monoanion, explicitly omitted from the work of Bunton and Shiner, does not yield a calculated secondary solvent kinetic isotope effect greater than about 0.6. The tentative conclusion to be drawn from such calculations is that the primary kinetic isotope effect = (experimental effect) \times (calculated secondary effect)⁻¹ is significantly larger than unity and conceivably is as large as 6, depending upon which acid is under consideration. So large a primary kinetic isotope effect would indicate a symmetric transition state with approximately equal OH bond strengths in the initial and final states.^{20,21} It is clear in any case that the experimental kinetic isotope data do not permit a decisive choice between a monoanion structure containing an intramolecular hydrogen bond and one that does not.

(22) E. M. Eyring, in preparation.

Solid-State Reactions of Bromine with Aromatic Hydrocarbons

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Contribution from the Chemistry Division, The Franklin Institute Research Laboratories, Philadelphia, Pennsylvania. 19103. Received June 28, 1965

Following a survey of the reactions of several solid aromatic hydrocarbons with bromine, a quantitative study was performed of the decomposition of a perylene-bromine charge-transfer complex in the solid state. The complex can be viewed as an intimate, stoichiometric mixture of reactants ordered at the molecular level. The reaction is first order to high conversion; at the lower temperatures, pure 3,9-dibromoperylene with no trace of monobromo or other dibromo derivatives is the product, but at -9°, some 3,10-dibromoperylene is obtained. The rates between 0 and -24° were measured; the half-life for the decomposition is 13 min. at 0°, and the activation energy is 10 kcal./mole. It is suggested that the solid state may serve as a useful matrix to exercise control of the rate, isomer distribution, and stereochemistry of many organic reactions.

Introduction

The operation of topochemical and topotactic forces in the reactions of organic solids has been established for certain photochemical reactions and polymerization systems.¹ Topochemical reactions are those in which

the process is dependent on the geometric arrangement of reactive groups within the lattice, and some notable examples are the photochemical dimerizations of substituted *trans*-cinnamic acids,² the photochromy of the anils,² and the solid-state polymerization of trioxane, diketene, and β -propiolactone.³ The term topotactic refers to solid-state reactions in which the product crystal orientation is related to that of the reagent. Some examples of topotactic reactions are the solid-state polymerizations of single crystals of trioxane³ and ϵ -aminocaproic acid,⁴ and the formation of oriented crystallites of N-phenylphthalimide from a single

(1) (a) For reviews of thermal reactions in the organic solid state, see H. Morawetz, "Physics and Chemistry of the Organic Solid State," D. Fox, M. M. Labes, and A. Weissberger, Ed., Interscience Publishers, John Wiley and Sons, Inc., New York, N. Y.: Vol. I, 1963, p. 287; Vol. II, 1965, p. 853. (b) For photochemical reactions, see H. S. A. Gilmour, *ibid.*, Vol. I, 1963, p. 329.

(2) M. D. Cohen and G. M. J. Schmidt, *J. Chem. Soc.*, 1996 (1964).

(3) K. Hayashi and S. Okamura, *Makromol. Chem.*, **47**, 230 (1961); K. Hayashi, Y. Kitamishi, M. Nishii, and S. Okamura, *ibid.*, **47**, 237 (1961); S. Okamura, K. Hayashi, and Y. Kitamishi, *J. Polymer Sci.*, **58**, 925 (1962).

(4) N. Morosoff, D. Lin, and H. Morawetz, *J. Am. Chem. Soc.*, **86**, 3167 (1964).

crystal of phthalanilic acid.⁵ It is of interest to examine how widespread is the influence of crystal structure on the course of solid-state chemical reactions. Both rates and isomer distributions should be sensitive to steric limitations and molecular orientations in a solid. Our initial attempt was to examine an aromatic substitution reaction, bromination of an aromatic hydrocarbon.

The bromination of anthracene in the solid state was noted in 1870.⁶ Further work on bromination of aromatic solids was conducted by Buckles, *et al.*,⁷ who studied a large group of aromatic compounds and found that substitution followed the course expected in solution bromination by an ionic mechanism. They viewed the reaction as occurring in either an absorbed phase or in a film of solution on the surface of the solid.

Synthesis of olefin dibromides *via* reaction of bromine vapor with solid aryl olefins has been reported.⁸ Recent work on addition reactions of bromine to aliphatic olefins at very low temperatures has also been conducted.^{8c} There is evidence that π complexes of bromine atoms and olefins are formed at -196° but that reaction does not occur until the melting point of the eutectic is reached.

Bromination in an aromatic solid charge-transfer complex was noted in 1956 when Akamatu, Inokuchi, and Matsunaga prepared charge-transfer complexes of hydrocarbons with halogens by exposing the solids to halogen vapor.⁹ They observed bromination occurring at a "moderate" rate while the complex of perylene with bromine is forming, and continuing after the complex is fully formed.

The study of the solid-state reaction of a charge-transfer (CT) complex to give a substitution product can be viewed as a rather advantageous solid-state situation of an intimate, stoichiometric mixture of reactants on a molecular level in which the course of the most probable reaction will reflect the minimum amount of atomic or molecular movement.

In order to delineate an appropriate reaction system for quantitative study, we first studied reactions of thin films of hydrocarbons with bromine vapor, and then focused on measuring the rate of reaction of perylene-bromine CT complex to give dibromoperylene.

Experimental Section

Gas-Solid Reactions. Thin films of aromatic hydrocarbons were cast on microscope slides by either solution evaporation or vapor deposition. These slides were then exposed to bromine, usually at room temperature *in vacuo* and/or in air. The weight gain in the slide was measured and in most cases spectroscopic or vapor phase chromatographic identifications were made of the major products.

Attaining reproducible rates of such a reaction was

(5) H. Morawetz, S. Z. Jakabhazy, J. B. Lando, and J. Shafer, *Proc. Natl. Acad. Sci. U. S.*, **49**, 789 (1963).

(6) C. Graebe and C. Liebermann, *Ann. Suppl.*, **7**, 257 (1870).

(7) R. E. Buckles, E. A. Hausman, and N. G. Wheeler, *J. Am. Chem. Soc.*, **72**, 2494 (1950).

(8) (a) A. Baeyer, *Ber.*, **13**, 2254 (1880); (b) K. Elbs and F. Bauer, *J. prakt. Chem.*, [2] **34**, 343 (1886); (c) J. J. Sudborough and K. J. Thompson, *J. Chem. Soc.*, **83**, 666 (1903); (d) F. Wohlring, *Ber.*, **47**, 108 (1914); (e) N. N. Semenov, *Pure Appl. Chem.*, **5**, 353 (1962), and references cited therein.

(9) H. Akamatu, H. Inokuchi, and Y. Matsunaga, *Bull. Chem. Soc. Japan*, **29**, 213 (1956).

attempted using thin film samples, single crystals or powders whose particle size were controlled by sieving procedures. For these studies, the thin films were deposited in a standard bell-jar type evaporator. The single crystals were hyperpure anthracene crystals which had been zone refined and grown from the melt. Round disks were prepared with the large parallel faces oriented either parallel or perpendicular to the AB (cleavage) plane. The faces were polished on benzene-soaked lens paper.

Solid-State Reactions. Preparation of the Perylene-Bromine Complex. A perylene-bromine complex in which no substitution occurs can be prepared at -77° in one of two ways: by the exposure of finely divided solid perylene to bromine vapor for long periods at -77° , followed by desorption of excess bromine by pumping; or by adding perylene in solvent to bromine in the same solvent at -77° . In the former case, the perylene turns black very rapidly; in the latter the black complex precipitates. When the material is held at this temperature, bromination proceeds at a negligible rate.

To attain a reproducible complex composition, it was found that the solution procedure was to be preferred. Preparations for kinetic studies were made as follows: 10-mg. portions of perylene were dissolved in 2 ml. of carbon disulfide. In each of six 20-ml. vials cooled to -77° was placed 0.2 ml. of bromine dissolved in 2 ml. of carbon disulfide. The perylene solutions were added very slowly to the cold bromine solutions. Solvent and excess bromine were removed from the vials using a circular vacuum manifold in which a liquid nitrogen cold finger was located equidistant from each vial. Approximately 3 hr. were required for all the free bromine to condense on the trap. The complex prepared in this way had a stable composition of perylene:bromine in a gram-atom ratio of $1:7 \pm 0.5$.

The particles of complex, when examined microscopically ($1000\times$ magnification) appeared as agglomerates varying in size from 1 to 100 μ of crystallites of $\sim 1\text{-}\mu$ diameter. As the black complex warmed up from -77° , no observable change in particle size of the individual crystallites could be observed.

Kinetics of the Solid-State Reaction. The individual aliquots of CT complex were allowed to react by heating to -24 , -9.2 , or 0° using Genetron 152A, Genetron 142B, or ice-water baths, respectively, while opening the vials to the atmosphere to allow hydrogen bromide evolution. The reaction was stopped by cooling to -77° . The remaining complex was decomposed by adding the contents of the vial to a solution of 2 g. of potassium iodide in 25 ml. of methanol at -77° . This solution was stirred until all the black particles had discharged their color. Per cent reaction was determined either titrimetrically or spectroscopically, the latter method being more convenient and giving the most reproducible results. The spectroscopic method involves determination of the extinction coefficients at 436 and 450 $m\mu$ for perylene and dibromoperylene, the latter being synthesized by a modification of Zinke's procedure.¹⁰

(10) A. Zinke and H. Trager, *Chem. Ber.*, **74**, 112 (1941).

Results

Gas-Solid Reactions. The reactions of hydrocarbon solids with bromine vapor is surprisingly facile for many compounds. Qualitative results were obtained on the products of the exposure of thin films of hydrocarbons cast on microscope slides to bromine at room temperature in air.

Naphthalene gives 1,4-dibromonaphthalene; anthracene forms initially 9,10-dibromoanthracene, but after ~ 1 hr. exposure gives 9,10-dibromo-1,2,3,4-tetrabromotetrahydroanthracene; and perylene yields 3,9- and 3,10-dibromoperylene. In 1 hr., a pyrene film adds six bromine atoms per mole, whereas a coronene film adds four bromine atoms per mole. Benzoic acid films give no reaction in 25 hr. at 50° .

The problem of attaining reproducible rate measurements for solid-gas reactions is a difficult one. We first considered the reaction of single crystal surfaces with bromine in some experiments using hyperpure anthracene crystals which had been zone refined and melt grown. Should such experiments be successful, one could obtain data which would help elucidate the influence of the structural anisotropy on reactivity. It has recently been reported that self-diffusion of anthracene is two to three times faster perpendicular to the *ab* plane than perpendicular to the *ac* plane,¹¹ and effects of iodine vapor on the conductivity of anthracene single crystals show a dependence on crystal orientation.¹² Preliminary experiments exposing single crystals to bromine vapor at room temperature showed no marked anisotropy, but it was impossible to obtain reproducible rates. In these experiments, surfaces of the crystal were solvent polished. To obtain meaningful data it would probably be necessary to study different surface preparation techniques until uniform structure of surface could be obtained.

Solid-State Reactions. Another approach to obtaining reproducible rates is to attempt to average the surface configuration by using a powdered sample. This approach was used to study the reaction of perylene with bromine in the form of the CT complex.

The chain-like structure of hydrocarbon-halogen complexes has been reported by Hassel¹³ for benzene-bromine and benzene-chlorine. In many donor-acceptor complexes, there is such alternation of the molecular components. Chemical reaction between the CT components, in such cases, involves conversion of an intimate, stoichiometric mixture into reaction products.

The perylene-bromine complex was prepared at -77° in the manner described above and had the composition 1 mole of perylene-7 g.-atoms of bromine. Long pumping would not remove further bromine. Unfortunately, neither the phase diagram for the system nor the crystal structure of the complex have been determined, and we cannot be sure that excess bromine is not present tightly held to a perylene-bromine complex of different stoichiometry. The phase diagram of the pyrene-iodine complex shows two distinct complexes of pyrene:iodine of compositions 2:1 and

(11) C. H. Lee, H. K. Kevorkian, P. J. Reucroft, and M. M. Labes, *J. Chem. Phys.*, **42**, 1406 (1965).

(12) M. M. Labes, O. N. Rudyj, and P. L. Kronick, *J. Am. Chem. Soc.*, **84**, 499 (1962); M. M. Labes and O. N. Rudyj, *ibid.*, **85**, 2055 (1963).

(13) O. Hassel, *Mol. Phys.*, **1**, 241, (1958); O. Hassel and H. Stromme, *Acta Chem. Scand.*, **13**, 1781, (1959).

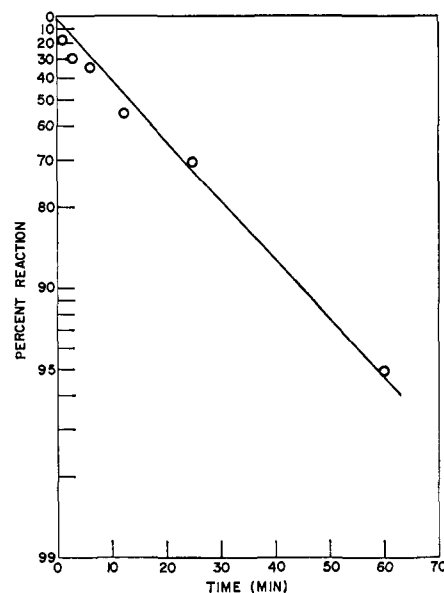


Figure 1. First-order plot for the solid-state decomposition of perylene- $[\text{Br}_2]_{3.5}$ at 0° .

1:2, respectively,¹⁴ of which the former is metastable. Perylene also forms several complexes, stable forms of perylene:iodine being reported 2:3¹⁴ as well as 1:3.¹⁵ The formation of a perylene-bromine complex of the observed composition is not unreasonable, since the crystal structure might accommodate more bromine atoms.

A kinetic procedure was established to study the reaction perylene- $[\text{Br}_2]_{3.5} \rightarrow$ dibromoperylene- $[\text{Br}_2]_{1.5} + 2\text{HBr}$. The product of the reaction of perylene and bromine in benzene at 30 – 40° is a mixture of 3,9- and 3,10-dibromoperylene complexed with bromine and hydrogen bromide. Vapor phase chromatographic analysis indicates the isomer ratio of the crude product to be 9:1 with the 3,9 isomer the major product. Under the conditions of our kinetic procedure, the product of the reaction was always pure 3,9-dibromoperylene at the lower temperatures, with no trace of the other isomer detectable *via* vapor phase chromatography. At -9° , however, the decomposition results in detectable concentrations of the 3,10 isomer.

Figure 1 presents a kinetic run at 0° . The reaction is first order to over 90% conversion with a half-life of 13 min. Rate constants at three temperatures are given in Table I; the kinetic data are difficult to obtain accurately, yet our reproducibility was about 10%. Plotting $\log k$ vs. $1/T$ ($^\circ\text{K}$.) gives a good Arrhenius relationship with an activation energy of 10.2 kcal./mole. The entropy of activation is calculated to be -37 e.u. With the limited amount of kinetic data available, however, these values are not known reliably.

In an attempt to obtain information on the structure of the perylene-bromine complex, the solid-state infrared spectrum at -140° from 1700 to 600 cm^{-1} was determined. The spectrum obtained is compared with those of perylene and 3,9-dibromoperylene in Figure 2,

(14) J. Kommandeur and F. R. Hall, *J. Chem. Phys.*, **34**, 129 (1961).

(15) M. M. Labes, R. Sehr, and M. Bose, "Proceedings of the International Conference on Semiconductor Physics," Prague, 1960, p. 850; R. Sehr, M. M. Labes, M. Bose, H. Ur, and F. Wilhelm, "Symposium on Electrical Conductivity in Organic Solids," John Wiley and Sons, Inc., New York, N. Y., 1961.

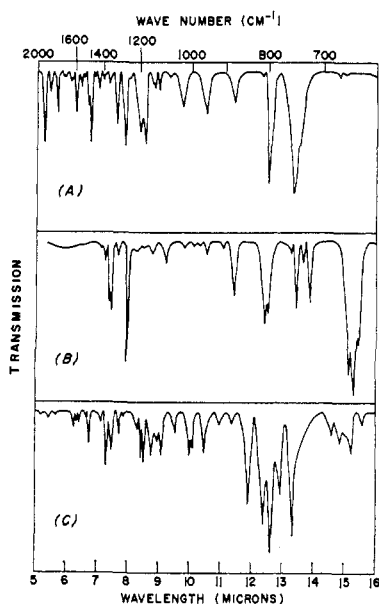


Figure 2. Infrared spectra of (a) perylene, (b) perylene- $[\text{Br}_2]_{3.5}$ at -140° , (c) 3,9-dibromoperylene.

and is quite different from that of either the parent hydrocarbon or the reaction product.

In contrast to this result, previous spectral studies of hydrocarbon-halogen complexes, which were confined to complexes of benzene and its alkyl derivatives,¹⁶⁻¹⁹

Table I. First-Order Rate Constants for Decomposition of Perylene- $[\text{Br}_2]_{3.5}$ Complex

Run no.	Temp., $^\circ\text{C}$.	$k \times 10^4$ sec. ⁻¹
1	-24	1.4
2	-24	1.4
3	-24	1.3
4	-9	3.4
5	-9	3.0
6	0	8.9

reveal only slight frequency changes but quite large intensity enhancements of weak bands already present in the donor molecule. This would be expected for a weak π complex between donor and acceptor involving only the π electrons of the donor. The spectrum of solid perylene-bromine complex differs from that of perylene by (a) the diminution of bands in the 1500-1600- cm^{-1} region where the C-C vibrations of an aromatic ring appear, (b) the presence of a very strong sharp band at 1252 cm^{-1} , and (c) the presence of many more bands in the 650-800- cm^{-1} region. The complex shows three very strong bands in the 650-675- cm^{-1} region which is completely empty in perylene; in the 700-800- cm^{-1} region perylene gives two strong bands characteristic of a 1,2,3-trisubstituted benzene but the complex gives, in addition to these two bands, two quite strong bands and two weak ones. Absorption in this region is dependent on the substitu-

- (16) E. E. Ferguson and F. A. Matsen, *J. Chem. Phys.*, **29**, 105 (1958); *J. Am. Chem. Soc.*, **82**, 3268 (1960).
 (17) E. E. Ferguson, *Spectrochim. Acta*, **10**, 123 (1957).
 (18) E. E. Ferguson, *J. chim. phys.*, **61**, 257 (1964).
 (19) R. S. Mulliken and W. B. Person, *Ann. Rev. Phys. Chem.*, **13**, 107 (1962).

tion in the aromatic rings, and therefore there must be a significant decrease in symmetry accompanying complex formation.

Insufficient evidence is available to decide between two possibilities. The decrease in symmetry is either due to close association of bromine to particular carbon atoms in the perylene rings (σ complex), or to a π complex in which the symmetry of some of the benzene rings in the system are sufficiently distorted to produce the observed complex frequency pattern. In an effort to distinguish between these possibilities, unsuccessful attempts were made to measure the solid-state infrared spectrum of the complex of bromine and 3,9-dibromoperylene, in which bromine does not further substitute, and of the perylene-iodine complex. In both cases, the complexes are completely opaque to infrared radiation, either by solid or mull sampling and by using both direct transmission and multiple internal reflection techniques. Attempts to measure the infrared spectra of halogen complexes of other aromatic hydrocarbons are being made.

Discussion

Thermal decomposition of crystalline organic solids is a very common phenomenon, but there has been little detailed study. This is because the process is generally far from simple. The products of the reaction may be liquids, solids, or gases. The reaction may initiate at crystal imperfections or surface centers. Yet there does not appear to be a case in which it has been clearly established that decomposition of an organic solid takes place entirely at the surface or at crystal imperfections.^{1,20} It certainly is the case that such processes, as well as reaction exclusively in associated liquid or gaseous phases, generally complicate the picture.

However, there are reactions which occur under the influence of the crystalline environments in which the structural consequences can be demonstrated. In addition to the photochemical and polymerization reactions already mentioned, it is a rather general observation that reactive species generated in a crystal can remain oriented with respect to the lattice for long periods of time. For example, the anisotropy of the e.p.r. spectrum of radicals generated by ionizing radiation in crystals is long lived, showing that this orientation persists,²¹⁻²³ and Pooley and Whiffen²⁴ observed that the two methylene hydrogens in the radical $\text{DOOC}\dot{\text{C}}\text{HCH}_2\text{COOD}$ differ in their chemical reactivity since they are crystallographically non-equivalent.

As a general rule, solid-state reactions are quite slow and often unobservable at temperatures well below the melting point. Those reactions that do occur usually involve (a) neighboring molecules dimerizing or polymerizing, (b) reactive intermediate trapping followed by recombination or reaction with the matrix, (c) isomerizations, (d) evolution of a gaseous fragment. The present study of a CT complex opens the possibility of conducting a wide variety of simple substitution re-

- (20) C. E. H. Bawn, "Chemistry of the Solid State," W. E. Garner, Ed., Butterworths, London, 1955, p. 254.
 (21) D. K. Gosh and D. H. Whiffen, *Mol. Phys.*, **2**, 285 (1959).
 (22) I. Miyagawa and W. Gordy, *J. Chem. Phys.*, **30**, 1590 (1959).
 (23) H. M. McConnell, C. Heller, T. Cole, and R. W. Fessenden, *J. Am. Chem. Soc.*, **82**, 766 (1960).
 (24) P. Pooley and D. H. Whiffen, *J. Chem. Soc.*, 366 (1962).

actions because the charge-transfer crystal orients the potential reactants with respect to one another. The first-order kinetics indicate that the subsequent reaction operates at the molecular level. No acceleration with time occurs; no "critical temperature" is observed. Instead the kinetics are first order to high per cent reaction, and a linear plot of $\log k$ vs. $1/T$ is obtained. At the lower temperatures, the product of the reaction is a pure isomer, with no trace of the other isomer or monobrominated product detectable *via* vapor phase chromatographic analyses.

Such observation of a unique product from a solid-state reaction is often evoked as proof that the crystal matrix controls the reaction. Schmidt clearly shows cinnamic acid dimer structure is correlated with monomer crystal structure.²⁵ Prelog, *et al.*,²⁶ recently observed that the decomposition of cyclodecyl tosylate in the solid state leads exclusively to *cis*-cyclodecene, while the reaction in the liquid phase yields 20% *cis* and 80% of the *trans* isomer. However, in our own studies, as well as in general, it is not usually possible to conduct a given reaction under the same conditions of temperature and concentration in both the solid and fluid (or solution) phases. It should be remembered that some of these effects may be rate or equilibrium controlled rather than crystal controlled. This is possibly the explanation for the observation that 3,10-dibromoperylene forms in detectable concentrations at -9° , but not at lower temperatures.

(25) G. M. J. Schmidt, *J. Chem. Soc.*, 2014 (1964).

(26) V. Prelog, W. Kung, and T. Tomljenovic, *Helv. Chim. Acta*, **45**, 1352 (1962).

The reaction under consideration is unusually fast for a solid-state reaction.¹ One interpretation of this is that the probability factor for collisions having the proper orientation for reaction is high in this solid matrix. The large negative entropy of activation implies that the transition state for this reaction is considerably more ordered than the ground state, but this entropy factor is not known reliably.

One of the most important problems in the field of electrophilic aromatic substitution in homogeneous solution is to decide the nature of the intermediate which, for example, Melander's work on isotope effects in aromatic substitution requires.²⁷ The view is that a typical substitution reaction occurs in two steps, with an intermediate forming which can, in principle, be isolated. It was one of our purposes to be able to comment on the nature of this intermediate. Although the perylene-bromine complex isolated in this work appears to be, from infrared data, a σ -type complex, we can neither definitely establish this nor be assured that the solid-state reactive species is identical with the reactive intermediate in solution.

The extent to which the solid matrix can be used to control the course of substitution reactions is currently being explored for a wide variety of aromatic derivatives entering into charge-transfer interactions and will be described in future publications.

Acknowledgment. The assistance of E. F. Chapman in performing some of the early experiments is acknowledged. This work was supported by the National Science Foundation under Grants GP1150 and GP3176.

(27) L. Melander, *Arkiv Kemi*, **2**, 211 (1951); "Isotope Effects on Reaction Rates," Ronald Press Co., New York, N. Y., 1960.

Comparative Stabilities of Gaseous Alane, Gallane, and Indane

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Contribution from the Laboratories Division, Aerospace Corporation, El Segundo, California. Received April 17, 1965

A technique is described for the mass spectrometric study of gaseous hydrides formed by atom reactions in a fast flow system. The relative abundances of alane, gallane, and indane formed in these reactions are used to classify the order of stability of these hydrides. The gases GaH₃ and InH₃ were found to be far less stable than AlH₃ despite the use of a wide range of reaction parameters. The implications of these results are discussed along with bond energetics in connection with the conflicting literature on the III-B metal hydrides. The present results support recent experimental observations concerning the instability and difficulty of preparation of liquid Ga₂H₆ and polymeric (GaH₃)_x in contrast to earlier reports of high stability and ready preparation.

Introduction

Wiberg and co-workers¹⁻³ have described the synthesis of a liquid Ga₂H₆ and the solid hydrides (GaH₃)_x

and (InH₃)_x. However, several recent studies^{4,5} have repudiated the validity of these syntheses, and the hydrides were shown to be far less stable than had been asserted. Since the present writers⁶ had been able to study mass spectrometrically the conditions governing the formation of gaseous AlH₃ and Al₂H₆ in a fast flow system of aluminum vapor and partially dissociated hydrogen, it was thought that an extension of this technique to the study of the analogous gaseous hydrides of the heavier III-B metals, Ga and In, would delineate the relative stabilities of the gaseous trihydrides of these metals and perhaps eliminate any lingering doubt about the claims of ref. 1-3. Al-

(1) E. Wiberg and T. Johannsen, *Naturwiss.*, **29**, 320 (1941).

(2) E. Wiberg and M. Schmidt, *Z. Naturforsch.*, **7b**, 577 (1952).

(3) E. Wiberg, O. Dittmann, and M. Schmidt, *ibid.*, **12b**, 57 (1957).

(4) D. F. Shriver, R. W. Parry, N. N. Greenwood, A. Storr, and M. G. H. Wallbridge, *Inorg. Chem.*, **2**, 867 (1963).

(5) N. N. Greenwood and M. G. H. Wallbridge, *J. Chem. Soc.*, 3912 (1963).

(6) P. Breisacher and B. Siegel, *J. Am. Chem. Soc.*, **86**, 5053 (1964).