and the heat content, and free energy functions of hydrogen,[9] naphthalene[10] and *cis*- and *trans*-decalins, the heat, free energy and equilibrium constants of various decalin reactions have been calculated as shown in Table IV. We did not find any published values of experimental measurements of these equilibria for comparison with our results.

BERKELEY, CALIFORNIA

[9] F. D. Rossini, *et al.*, "Selected Values of Physical and Thermodynamic Properties of Hydrocarbons and Related Compounds," Carnegie Press, Pittsburgh, 1953.

[10] A. L. McClellan and G. C. Pimentel, *J. Chem. Phys.*, **23**, 245 (1955).

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF CALIFORNIA, BERKELEY]

Reaction Kinetics by the Matrix Isolation Method: Diffusion in Argon; *cis–trans* Isomerization of Nitrous Acid

BY GEORGE C. PIMENTEL

RECEIVED JUNE 5, 1957

The use of the matrix isolation technique for the study of reaction rates of chemical reactions with heats of activation as low as one or two kcal. is described. Reactions which might be studied include isomerization, bond rupture, bond formation reactions and the process of diffusion in the solid matrix. A crude estimate of the rate of diffusion of ammonia in solid argon is presented. The heat of activation of the isomerization of *cis*-HNO_2 to *trans*-HNO_2 was measured at 20°K. in solid nitrogen and found to be much lower than current estimates.

The matrix isolation method, as proposed by Whittle, Dows and Pimentel,[1] involves the deliberate suspension of reactive molecules in a rigid and inert solid matrix for the purpose of spectroscopic study of these molecules. It is the purpose of this paper to note that the technique not only provides a means of keeping reactive molecules apart but also a method of bringing them *together* under unusual environmental conditions. In particular, two reactive molecules can be formed together (*e.g.*, by photolysis) or brought together (*e.g.*, by diffusion in the solid) at extremely low temperatures where measurable reaction rates will be observed even for free energies of activation of the order of one or two kilocalories, a range relatively inaccessible to measurement by other methods. In this paper the experimental technique is described, examples are cited, and difficulties of interpretation are discussed.

Proposed Experimental Procedure.—In this Laboratory, the process of diffusion of a molecule A suspended in a matrix M[2] has been studied. The temperature at which such a diffusion process becomes rapid seems to be around three to five tenths of the melting point of the pure matrix. Thus a molecule such as NO_2, H_2O or NH_3 diffuses rapidly in solid argon (T_m = 83.8°K.) at temperatures above 35°K. Hence reactive molecules can be brought together in solid argon in a period of a few seconds at 40–50°K. and thereafter their fates can be studied spectroscopically as a function of time. Other matrix materials can be used to obtain either higher or lower diffusional temperatures.

Reaction Processes in the Matrix.—Of the possible reactions which might take place under the proposed conditions, the simplest type would be the first-order deactivation of an excited state, *e.g.*, a state involving conformational or tautomeric excitation. In the former case, the rate of formation of the most stable isomer would be determined by the potential function which governs the intramolecular movement, for example, a potential barrier hindering internal rotation. (Entropy effects will be discussed later.) In the case of tautomers, the process would be governed by the properties of the transition state in intramolecular rearrangement. If the confines of the matrix impede intramolecular movements, the measured heat of activation probably will exceed that of the gaseous molecule.

Bond rupture reactions would also be of first order. The effect of the matrix cage on $\Delta H^{\ddagger}$ would depend upon the dimension along the reaction coördinate of the activated state, $r^{\ddagger}_{AB}$, compared to the size of the matrix cage. If the cage is small compared to $r^{\ddagger}_{AB}$, then $\Delta H^{\ddagger}$ will be influenced by the heat of activation of diffusion, $\Delta H^{\ddagger}_{D}$, the heat of activation for reaction in the gas phase, $\Delta H^{\ddagger}_{0}$, and the heat of reaction, ΔH_R. Situations which are readily interpreted are the special cases: (1) $\Delta H^{\ddagger} >> \Delta H^{\ddagger}_{D}$; (2) $\Delta H^{\ddagger}_{D} >> \Delta H^{\ddagger}_{0}$ and $r^{\ddagger}_{AB}$ comparable to the cage size; and (3) of $r^{\ddagger}_{AB}$ small compared to the cage size. In case (1) the value of $\Delta H^{\ddagger}$ measured is little influenced by the matrix and in case (2) the measured $\Delta H^{\ddagger}$ is approximately $\Delta H^{\ddagger}_{D}$. In case (3) the potential curve applicable to the gas phase, curve a in Fig. 1, may be influenced somewhat by the matrix cage, as suggested by curves b and c in Fig. 1. Again the measured activation enthalpy should exceed the gas phase $\Delta H^{\ddagger}_{0}$.

Reactions involving bond formation are also influenced by cage size. However, in either case (1) or (2) the reaction kinetics become of second order. In case (3) it is possible for the reaction to occur within the cage and at a temperature at which diffusion cannot take place. If a potential curve such as curve b of Fig. 2 were applicable, the kinetics would be first order because the reactive species are held together by the matrix. In a favorable case, where the cage is very large compared to $r^{\ddagger}_{AB}$, $\Delta H^{\ddagger}$ would provide an estimate of $\Delta H^{\ddagger}_{0}$.

A fourth type of reaction, diffusion, can be studied. The rate can be determined by observing the disappearance of a suitable suspended species which reacts with low $\Delta F^{\ddagger}$.

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[1] E. Whittle, D. A. Dows and G. C. Pimentel, *J. Chem. Phys.*, **22**, 1943 (1954).

[2] E. D. Becker and G. C. Pimentel, *ibid.*, **25**, 224 (1956).

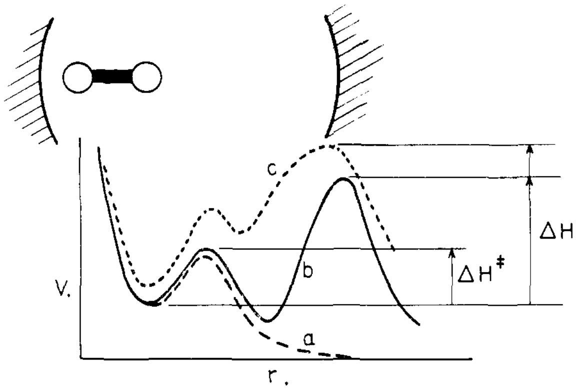

Fig. 1.—Potential curve for bond rupture within the matrix cage: r = reaction coördinate; (a) possible potential curve applicable to a gas phase reaction; (b, c) possible potential curves as modified by constraints of the matrix.

Entropy of Activation.—The matrix isolation technique has been used effectively at temperatures below 100°K. and, in these laboratories, mainly in the range 4–40°K. At these low temperatures the entropy of activation in first-order reactions is undoubtedly very close to zero.

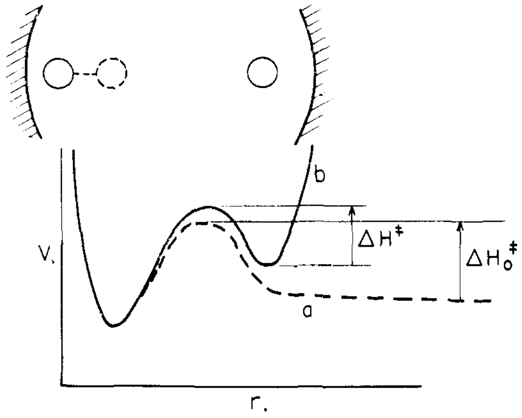

Fig. 2.—Potential curve for bond formation within the matrix cage: r = reaction coördinate; (a) possible potential curve applicable to a gas phase reaction; (b) possible potential curve as modified by constraints of the matrix.

In second-order reactions the concentration units selected for the standard state will influence the value of $\Delta S^{0\ddagger}$, mole fraction units being convenient. The form of the standard state appropriate to the experiment is, no doubt, the glassy state. Hence $\Delta S^{0\ddagger}$ will not approach zero as the temperature approaches zero (as it would, by the third law of thermodynamics, if the standard states were perfect crystals). Nevertheless $\Delta S^{0\ddagger}$ is expected to be low at temperatures below 50°C. and possibly negligible.

Heat of Activation.—The familiar reaction rate expression for the rate constant k_1 or k_2 applies in most cases.

$$k_{1,2} = \frac{kT}{h}\, e^{\Delta S^{0\ddagger}/R} e^{-\Delta H^{0\ddagger}/RT} \qquad (1)$$

For rotational isomerization reactions the activated state involves rotational movement rather than a translation. Hence the kT/h factor may require modification.

Experimental

The studies reported here were conducted as described in reference 2 except for the photolysis, which was conducted as described in reference 3.

Two specific experiments provide interesting examples. The first experiment, A, involved a mixture of NH_3 gas in argon at a mole ratio of argon/ammonia of 195. The mixture was frozen at 20°K. and the infrared spectrum indicated that a fraction of the ammonia was in the form of monomeric NH_3. The temperature was allowed to rise at a rate of about 0.1 degree/second. Two spectra taken 75 seconds apart revealed the disappearance of about 88 ± 6% of the monomer (with the growth of the spectral features of hydrogen bonded polymers). During this 75-second period, the temperature varied from 40 to 47°K.

In experiment B, nitrogen gas containing both HN_3 and oxygen was frozen at 20°K. The mole ratios were N_2:HN_3:O_2 = 500:1:x where x was in one experiment 0.5 and other experiments at least 2. After an infrared spectrum was recorded, the mixture was photolyzed for 13–30 minutes. The spectrum was then recorded as a function of time at a recorded window temperature of 20°K. A well-defined spectral feature at 868 cm.$^{-1}$ which appeared during photolysis was observed to disappear, while the absorption at an adjacent spectral feature at 818 cm.$^{-1}$ increased somewhat, as shown in Fig. 3. Two experiments form the basis of the estimate that 42 ± 5% of the feature at 868 cm.$^{-1}$ was lost in 25 minutes. The temperature was measured by a copper–constantan thermocouple embedded in the salt window bearing the sample. It is believed that the sample temperature was in the range 20–23°K.

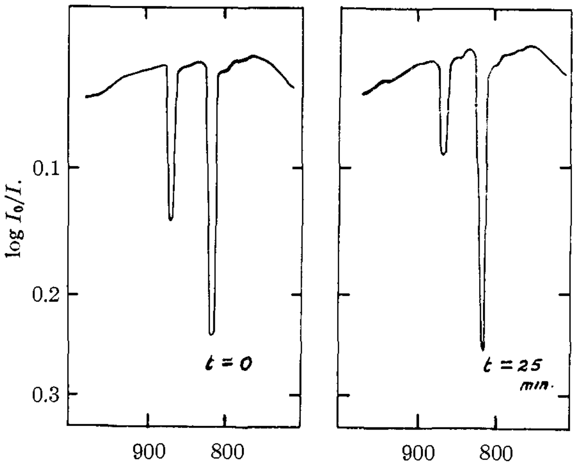

Fig. 3.—Spectra of photolysis products of HN_3 in argon; T = 20°K.; oxygen present.

A. Diffusion of Ammonia in Solid Argon.—In this experiment the rate of disappearance of ammonia was measured over a temperature interval of 40 to 47°K. Assuming equation 1 is applicable, that the temperature was 43.5°K., and that the polymer concentration was large enough to be effectively constant, we calculate $\Delta F^{\ddagger} \sim 2$ kcal./mole. This crude estimate is considered to apply to the diffusional process since it is expected that $\Delta H^{\ddagger}$ of hydrogen bond formation is zero. It is possibly fortuitous that the calculated $\Delta F^{\ddagger}$ is only about 500 calories below the $\Delta H^{\ddagger}$ of self-diffusion predicted from the melting point of argon and the empirical relation $\Delta H^{\ddagger} = cT_m$ (c = 28–32) observed for self-diffusion in cubic close packed metals[4,5] (argon crystallizes in a cubic close packed structure).

B. The Rotational Isomerization of HNO_2.—In this experiment a species was produced by photolysis and its rate of disappearance was examined spectroscopically at a constant matrix temperature near 20°K. At this temperature, diffusion of even diatomic species has been found to be negligible.[2] Hence the process is presumed to be governed

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(3) E. D. Becker, G. C. Pimentel and M. Van Thiel, *J. Chem. Phys.*, **26**, 145 (1957).

(4) J. Van Liempt, *Z. Physik*, **96**, 534 (1935).

(5) N. H. Nachtrieb, J. A. Weil, E. Catalano and A. W. Lawson, *J. Chem. Phys.*, **20**, 1189 (1952).

by first-order kinetics. The temperature is taken to be 21.5 ± 1.5°K. If equation 1 is applicable and if $\Delta S^{\circ\ddagger} = 0$, then the disappearance of the band at 865 cm.$^{-1}$ is governed by a process with a heat of activation of 1500 ± 130 cal.

The two features which vary with time, 868 and 818 cm.$^{-1}$, are assigned, respectively, to the *cis* and *trans* forms of nitrous acid, HNO_2. This species is presumed to form in the reactions 2, 3 and 4, followed by 5.

$$HN_3 + h\nu = NH + N_2 \qquad (2)$$

$$NH + O_2 = HONO\ (trans) \qquad (3)$$

$$NH + O_2 = HONO\ (cis) \qquad (4)$$

$$HONO\ (cis) = HONO\ (trans) \qquad (5)$$

The identification is supported by the vibrational assignment proposed by earlier workers.[6,7] They assign the intense absorptions at 856 and 794 cm.$^{-1}$ to the O–N stretching modes of the gaseous *cis* and *trans* isomers, respectively. The energy of the *cis* form is 506 ± 250 cal./mole above the *trans* form.[7] Jones, *et al.*, estimate the barrier to internal rotation to be about 12 kcal./mole.[7] More recently but without new data Palm[8] has expressed agreement with this estimate. It is not possible to rationalize a 12 kcal. barrier with the measured rate either by adjustment of $\Delta S^{\circ\ddagger}$ or of the (kT/h) factor. It is possible but unlikely that the reaction under study is not the *cis–trans* isomerization of HNO_2. More detailed studies of this system are in progress, both to corroborate the assignment and to measure $\Delta S^{\circ\ddagger}$.

Conclusion

It is clear that the matrix isolation technique offers unique possibilities in the study of reaction kinetics. There are limitations and difficulties of interpretation whose importance cannot be evaluated without more experience. The most serious of these is probably that the matrix may influence the activation thermodynamics of the reactions studied. Nevertheless it seems likely that the method will prove to be a valuable tool for the study of extremely fast reactions, including the reactions of free radicals.

Acknowledgment.[9]—The author wishes to thank Professor Robert E. Connick for many helpful and critical discussions.

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[6] L. D'or and P. Tarte, *Bull. Soc. Roy. Sci., Liège*, 478 (1951).

[7] L. H. Jones, R. M. Badger and G. E. Moore, *J. Chem. Phys.*, **19**, 1599 (1951).

[8] A. Palm, *ibid.*, **26**, 855 (1957).

[9] The research described was supported in part by the American Petroleum Institute, Research Project 50, and by the United States Air Force through the AFOSR of the Air Research and Development Command, under Contract No. 49(638)-1. Reproduction in whole or in part is permitted for any purpose of the U. S. Government.

BERKELEY, CALIF.

[CONTRIBUTION FROM THE DEPARTMENT OF BIOCHEMISTRY, COLLEGE OF PHYSICIANS AND SURGEONS, COLUMBIA UNIVERSITY]

The Catalysis of the H_2–D_2O Exchange by Aqueous Buffer Solutions[1]

BY S. L. MILLER AND D. RITTENBERG

RECEIVED AUGUST 9, 1957

The exchange between molecular hydrogen and D_2O is known to be catalyzed by hydroxide ion and follows the rate law[3] $d(P_{HD})/dt = k(P_{H_2})(OH^-)$. The exchange has been investigated at lower pH values in the temperature range 110–190° using borate, phosphate, glycine, succinate and acetate buffers. The same rate law is obeyed provided the OH^- concentration measured at 25° is corrected for the change in the pK of the acid and the pK of the water at the higher temperatures. The heat of activation is 28 ± 3 kcal. Neither dilute nor concentrated acids catalyze the exchange.

During an investigation of the catalysis by various compounds of the H_2–D_2O exchange reaction, it was necessary to correct for the exchange reaction which occurs in the absence of added catalysts. It is known that hydroxide ion will catalyze the exchange.[2] More recently[3] an investigation of the mechanism has shown that the rate of exchange is proportional to the pressure of hydrogen gas and the OH^- concentration in the range 0.1 to 1 *M*. An extension of the exchange experiments to lower values of pH is reported in this paper.

Experimental

The exchange reactions were carried out in Pyrex tubes of about 3-ml. capacity with a break seal at one end. 0.5 ml. of buffer and 0.5 ml. of D_2O were placed in the tube, and the gas phase replaced by hydrogen. The reaction tubes were kept at a constant temperature (±1°) in an oven which was rocked about 10 times per minute. After various time intervals the deuterium concentration of the gas phase was determined by mass spectrometric analysis. The average of the initial and final pH values was taken as the pH of the system. The data were reproducible within ±5%.

Consider a system in which the gas phase initially contains H_2, and the aqueous phase contains D_2O of mole fraction N_D. If the exchange is catalyzed only by hydroxide ion, the rate law is

$$d(HD)_l/dt = kN_D(OH^-)(H_2)_l \qquad (1)$$

where k is expressed in liters mole^{-1} hr.$^{-1}$, $(HD)_l$ and $(H_2)_l$ are the molar concentrations of these gas species in solution. This equation ignores the isotope effect between H_2O and D_2O, but it can be included in the constant N_D. Let V_l be the volume of solution, V_g the volume of gas, K_s the constant of Henry's law, P_{H_2} the partial pressure of H_2. We will consider the case where the reaction proceeds only to a small extent. The number of moles of HD, n_{HD}, produced after t hours in V_l liters of solution is obtained by integrating eq. 1 to give

$$n_{HD} = kN_D\,(OH^-)K_sP_{H_2}V_lt$$

The HD produced in solution is mixed with the $P_{H_2}V_g/RT$ moles of H_2 in the gas phase, therefore, the ratio of HD to H_2 in the gas phase after t hours is

$$(HD/H_2)_g = kN_DK_s(OH^-)\,RT(V_l/V_g)_t$$

or

$$(HD/H_2)_g = k'(OH^-)(V_l/V_g)t \qquad (2)$$

where $k' = kN_DK_sRT$. This equation requires that the rate of increase of HD/H_2 be independent of the pressure of the hydrogen, proportional to the ratio of the liquid to gas volumes, and proportional to the concentration of hydroxide ion if the exchange is catalyzed only by hydroxide ion.

Since the experiments were carried out at temperatures above 100° it was necessary to calculate the hydroxide ion

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[1] This research was supported by Atomic Energy Commission Contract #AT(30-1)1803 to Columbia University.

[2] K. Wirtz and K. F. Bonhoeffer, *Z. physik. Chem.*, **177A**, 1 (1936).

[3] W. K. Wilmarth, J. C. Dayton and J. M. Flournoy, THIS JOURNAL, **75**, 4549 (1953).