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of temperature over the range 623–793°K. From the experimental results, the following equation has been derived

$$\rho_{\text{Sn}} = 7.819 - 2.104(10^{-3})T + 9.6(10^{-7})T^2$$

The density of a liquid alloy containing 4% palladium was also determined as 6.965 g/cm³ at 785°K. The density of pure tin at this temperature is 6.759 g/cm³, and the density of a mechanical mixture containing 4% palladium, calculated from accepted atomic diameters,¹⁰ would be 6.804 g/cm³. Thus the increase in density due to adding 4% palladium to liquid tin is more than four times what would be expected from a mechanical mixture of the two elements. This again confirms the existence of strong bonding between the palladium and tin atoms in the liquid.

From the experimental density data, it has been possible to calculate the palladium–tin interatomic distance, using a model based on the following assumptions. (a) The molecular species formed is PdSn₄. (b) The molecules are tetrahedral, with four tins surrounding a central palladium atom. This is the simplest form for a molecule of such composition. (c) The molecules are spherical.

This model yields a Pd–Sn distance of 2.70 Å, which is in close agreement with the values for the intermetallic compounds. This value is also listed in Table III.

Summary

The lack of direct methods of determining the structure of liquid palladium–tin alloys makes it necessary to postulate a structure, derive various properties from this model, and compare the derived properties with those measured experimentally. In order for the model to be considered valid, complete agreement must exist between derived and measured properties in all cases. At the present stage of development, neither theoretical nor experimental data are available in sufficient quantity and with sufficient precision to permit complete quantitative comparison. Therefore, the conclusions presented here must be considered tentative, subject to proof by further investigation.

From the evidence available, it appears that tin-rich liquid palladium–tin alloys, at temperatures between 600 and 800°K and at compositions ranging from pure tin up to the liquidus, consist of molecules composed of both palladium and tin atoms, these molecules being in equilibrium solution in a matrix of pure tin. While the exact composition of the molecules has not been conclusively determined, it is most probable that they fit the formula PdSn₄.

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(10) C. S. Barrett and T. B. Massalski, "Structure of Metals," 3rd ed, McGraw-Hill Book Co., Inc., New York, N. Y., 1966, p 628.

Arrhenius Parameters for the Reactions of Atomic Nitrogen with Some Olefins and Acetylenes

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The rates of reaction of atomic nitrogen, produced in a flow system by means of a microwave discharge, with a series of olefins and acetylenes have been measured from 320 to 550°K. Preexponential factors and activation energies have been derived. In addition, upper limits are given for the rates of reaction of atomic nitrogen with several miscellaneous organic compounds.

Introduction

An earlier article from this laboratory reported rate constants at 340°K for the reactions of atomic nitrogen with a series of olefins.¹ These measurements have now been repeated over the temperature interval

320–550°K and have been extended to include data on a series of acetylenes and some miscellaneous compounds.

(1) J. T. Herron, *J. Phys. Chem.*, **70**, 2803 (1966).

Experimental Section

The experimental approach, which was to couple a discharge-flow system to a mass spectrometer to permit the direct measurement of the partial pressures of reactants and products, has been described in detail elsewhere.^{1,2}

In the present work the reactor was a 20 mm i.d. Pyrex tube which could be heated to 550°K. The total pressure was about 2.5 torr. Reaction time, which could be adjusted by changing the distance between the reactant inlet and the sampling orifice of the mass spectrometer, was normally about 0.02 sec.

As noted previously,¹ secondary reactions, particularly of atomic hydrogen, necessitate working at very low reactant flows where the degree of conversion is small (e.g., 2–10%). At higher flows, reaction products cause additional reaction, leading to an apparent increase in rate constant. We have in all cases varied the initial partial pressures of the reactants over about a threefold range to be sure that our data were not complicated by secondary reactions. Under these conditions atomic nitrogen is in great excess, and the rate of the reaction is given by

$$k = \ln(R_0/R) / \int_0^t (N) dt \quad (1)$$

where R_0 and R are the partial pressures of the reactants at times zero and t , respectively, and (N) is the atomic nitrogen concentration. Under our experimental conditions, loss of atomic nitrogen due to reaction or homogeneous recombination is negligible, the only significant loss mechanism being recombination on the walls of the reactor.

The atomic nitrogen partial pressure along the reaction tube was measured by titration with nitric oxide,³ which also served to put the directly measured nitrogen atom partial pressure on an absolute basis.

The observed rate of decay of atomic nitrogen was sufficiently small so that the quantity $\int_0^t (N) dt$ in eq 1 could be replaced by $(N)_{av}t$, where $(N)_{av}$ is the average nitrogen atom concentration.⁴ The latter typically corresponded to a partial pressure of about 0.005 torr.

When the reactor was operated at high temperatures, considerable outgassing occurred in the ion-source region of the mass spectrometer. This was reflected in a very great increase in background signal, which was particularly serious at masses less than 45.

In the case of ethylene and propene, this problem was avoided by using trideuterioethylene and hexadeuteriopropene, the parent ions of which are free from background interference. The measured rates will, therefore, reflect any kinetic isotope effects, although no effect was observed in a previous comparison of the propene and hexadeuteriopropene rate constants at 340°K.¹

At least ten rate measurements were made for each compound studied. Assuming that the Arrhenius equation $k = A \exp(-E/RT)$ was applicable to these data, the parameters A and E , as given in Table I, were evaluated from a plot of $\log k$ vs. $1/T$. Computed uncertainties are standard deviations based on a least-squares treatment of the data. A plot of the deviations of the points from the computed line showed a random distribution, with no evidence of curvature.

Table I: Arrhenius Parameters for the Reactions of Atomic Nitrogen with Some Olefins and Acetylenes^a

Reactant	Log A , cm ³ mol ⁻¹ sec ⁻¹	E , cal mol ⁻¹
Olefins		
Ethylene, C ₂ H ₄	10.425 ± 0.208	760 ± 380
Ethylene ^b	10.204	700
Ethylene ^c	11.394	1900
Isobutene	10.893 ± 0.154	550 ± 270
Propene, C ₃ H ₆	10.948 ± 0.145	1020 ± 270
Propene ^b	11.176	1650
2-Methyl-2-butene	10.966 ± 0.140	860 ± 250
1-Butene	11.190 ± 0.129	1310 ± 230
2,3-Dimethyl-2-butene	11.226 ± 0.099	1370 ± 170
cis-2-Butene	11.369 ± 0.082	1980 ± 150
trans-2-Butene	11.525 ± 0.071	2100 ± 125
Acetylenes		
Acetylene ^d
Propyne	10.839 ± 0.153	1480 ± 280
2-Butyne	11.265 ± 0.133	1840 ± 250
1-Pentyne	11.468 ± 0.163	2080 ± 300
3-Hexyne	11.526 ± 0.122	2190 ± 220
1-Butyne	11.539 ± 0.114	2240 ± 210
1-Hexyne	11.664 ± 0.130	2450 ± 240

^a This work, except as noted. ^b G. Paraskevopoulos and C. A. Winkler, *J. Phys. Chem.*, **71**, 947 (1967). ^c L. I. Avramenko and V. M. Krasnen'kov, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 600 (1964). A and E were recomputed from the original data. ^d From 330 to 550°K, $k \leq 2 \times 10^9$ cm³ mol⁻¹ sec⁻¹. L. I. Avramenko and V. M. Krasnen'kov, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 822 (1964), give $k = (5.4 \times 10^9)T^{1/2} \exp[(-2300 \pm 299)/RT]$ cm³ mol⁻¹ sec⁻¹. At 550°K this leads to a rate constant approximately equal to our limiting value.

Results and Discussion

Arrhenius parameters for the reactions of atomic nitrogen with olefins and acetylenes are summarized in Table I. Our results are in good agreement with those of Paraskevopoulos and Winkler⁵ for ethylene and

(2) F. S. Klein and J. T. Herron, *J. Chem. Phys.*, **41**, 1285 (1964).

(3) G. B. Kistiakowsky and G. G. Volpi, *ibid.*, **28**, 665 (1958).

(4) Assuming a first-order decay of atomic nitrogen, we calculate a recombination coefficient $\gamma = 2 \times 10^{-4}$ at 320 and 550°K. This value agrees quite well with $\gamma(\text{quartz}) = 5.5 \times 10^{-4}$ at 300°K reported by K. M. Evenson and D. S. Burch, *J. Chem. Phys.*, **45**, 2450 (1966).

(5) G. Paraskevopoulos and C. A. Winkler, *J. Phys. Chem.*, **71**, 947 (1967).

propene but differ from those of Avramenko and Krasnen'kov⁶ for the ethylene reaction. However, as can be seen from the table, our data for ethylene are of poor precision and it is difficult to compare them with the results of other workers, particularly in those cases where no indication of precision is given.

In the experiments of Paraskevopoulos and Winkler, the reaction was stopped at various times by means of a movable catalytic probe, and the rate constant was calculated from the over-all stoichiometry on the assumption that the hydrogen cyanide produced in the reaction was proportional to the atomic nitrogen consumed. Although the reaction is almost certainly so complex that the latter assumption is not strictly valid,⁷ it does not appear to introduce any gross errors into the rate measurements.

Avramenko and Krasnen'kov base their rate measurements on the variation of product yield with reactant flow using a reactor having the walls coated with TiO₂. The assumptions required to derive rate data from this type of experiment are so open to question that it is difficult to have much confidence in their results.

The reactions of atomic nitrogen (⁴S) with olefins and acetylenes to yield products in their ground electronic states are spin forbidden, and therefore the low *A* factors for these reactions are not unexpected.⁸ Examination of the data of Table I does not reveal any obvious correlation between Arrhenius parameters and molecular structure. The only regularity in the data is the approximately linear dependence of the activation energy *E* on the preexponential factor *A*, which is the basis for ordering the data of Table I.

In addition to acetylene, we have found no measurable degree of reaction for CH₄, CH₃F, CH₃Cl, C₂HCl₃, *trans*-2-C₄F₈, and C₆H₆ (benzene). For these reactants, we estimate that at 500°K, *k* ≤ 4 × 10⁹ cm³ mol⁻¹ sec⁻¹. Although C₂H₅Cl and C₂H₅Br appeared to react at a rate comparable to that of ethylene, we have not studied these reactions in any detail.

The low degree of reactivity of atomic nitrogen suggests that these reactions could be initiated by highly reactive species, such as N(²S), N₂(³Σ_u⁺), H, or O, produced in extremely minute quantities in the electrical discharge. However, evidence to support such a position has not been forthcoming. We have argued previously against atomic hydrogen or oxygen being

the initiating species,¹ and Starr and Shaw⁹ have summarized the arguments against metastable nitrogen species originating in the discharge itself.¹⁰ However, Campbell and Thrush¹¹ have now shown that N₂(³Σ_u⁺) produced by the recombination of nitrogen atoms reacts with CO₂, NH₃, and N₂O. Furthermore, they have shown that the rate of reaction is directly proportional to the total pressure and to the square of the nitrogen atom partial pressure. We have attempted to observe similar rate dependencies in our work, with the results being shown in Table II. We find the rate constant to be essentially independent of initial atom concentration, time, or total pressure. If N₂(³Σ_u⁺) were the initiating species, then we should expect that our observed rate constant would be directly proportional to (N)*P*_{total}, which clearly is not the case.

Table II: Rate Constant for the Reaction of Atomic Nitrogen with *trans*-2-Butene as a Function of Initial Atomic Nitrogen Partial Pressure, Total Pressure, and Reaction Time

<i>T</i> , °K	10%, sec	<i>P</i> _{total} , torr	10 ³ <i>P</i> <i>N</i> , torr	Relative <i>P</i> <i>N</i> / <i>P</i> _{total}	10 ⁻¹⁰ <i>k</i> , cm ³ mol ⁻¹ sec ⁻¹
319	16.7	1.77	3.57	1.0	1.19
319	24.7	2.62	5.68	2.4	1.35
337	22.8	2.90	5.51	2.5	1.55
319	38.0	4.03	5.15	3.3	1.36
337	22.8	2.90	7.43	3.4	1.42
364	16.0	4.17	11.3	7.5	1.31

Furthermore, we may note that if atomic hydrogen or oxygen were the initiating species, they would probably just as readily react with C₂H₂, C₂HCl₃, and *trans*-2-C₄F₈ as with any other unsaturated compound. Their lack of reactivity supports the conclusion that the reaction is not initiated by atomic hydrogen or oxygen.

(6) L. I. Avramenko and V. M. Krasnen'kov, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 600 (1964).

(7) J. T. Herron, *J. Phys. Chem.*, **69**, 2736 (1965).

(8) H. G. V. Evans and C. A. Winkler, *Can. J. Chem.*, **34**, 1217 (1956).

(9) W. L. Starr and T. M. Shaw, *J. Chem. Phys.*, **44**, 4181 (1966).

(10) The arguments with respect to atomic hydrogen or oxygen apply only to the olefin reactions, inasmuch as they were partly based on a knowledge of the corresponding atomic hydrogen and oxygen rate constants. The equivalent data are not available for the acetylene reactions.

(11) I. M. Campbell and B. A. Thrush, *Chem. Commun.*, 932 (1967).