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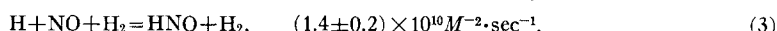
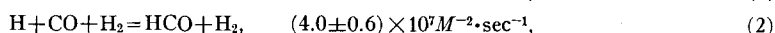
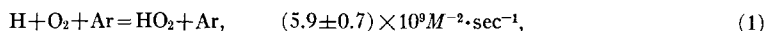
Pulse Radiolysis Studies. XX. Kinetics of Some Addition Reactions of Gaseous Hydrogen Atoms by Fast Lyman- α Absorption Spectrophotometry*

T. HIKIDA, J. A. EYRE, AND LEON M. DORFMAN

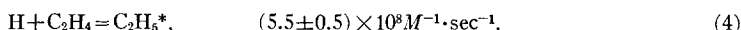
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The pulse radiolysis technique combined with fast Lyman- α absorption spectrophotometry, has been used to study the kinetics of several addition reactions of gaseous hydrogen atoms. The following absolute rate constants, at 298°K, have been obtained:



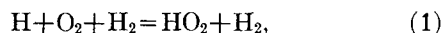
These results, and our earlier value for k_1 with H_2 as third body, give values of $k_1\text{H}_2/k_1\text{Ar} = 2.9$ and $k_2\text{H}_2/k_2\text{Ar} = 1.5$ for the relative third-body efficiencies of hydrogen and argon. The high-pressure limiting rate constant for H-atom addition to ethylene, obtained directly in the high-pressure region, was found to be



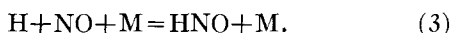
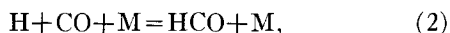
with both H_2 and Ar as third body.

INTRODUCTION

The combined techniques of pulse radiolysis, to produce ground-state hydrogen atoms, and fast spectrophotometric absorption measurement of the Lyman- α resonance radiation (1215.7 Å), to detect these atoms, have been used to study a number of gas phase addition reactions of H atoms. This method, fully described in our earlier report¹ on the reaction

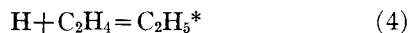


has now been extended to an investigation of the reactions



The data obtained provide absolute rate constants as well as information about the relative efficiencies of H_2 and Ar as a third body.

This fast reaction method has also been used to determine directly the high-pressure limiting rate constant, as outlined in a preliminary report,² for the reaction



at pressures sufficiently high for complete collisional de-excitation of the vibrationally excited ethyl radical.

In the course of this work, a direct test of the validity of Beer's law in the use of the Lyman- α line in our system has been carried out by using repetitive electron pulses to build up integral multiples of the initial hydrogen atom concentration in hydrogen gas.

EXPERIMENTAL

Pulse Source

Hydrogen atoms were produced in hydrogen gas by a high current pulse of high energy electrons from an

electron accelerator. The accelerator used in all the kinetic studies was a Febetron Model 706 pulsed electron accelerator, which uses a Marx surge circuit to produce a pulse of 0.5-MV electrons with a time profile that is 3 nsec wide at the half-height and 10 nsec wide at the base. This time range is more than two orders of magnitude smaller than the time resolution required for the kinetic studies. The pulse current is about 7000 A, so that the pulse carries about 10 J of energy, only a small fraction of which is absorbed in the gas. Pulse intensity was reproducible to the extent of about $\pm 3\%$.

For the experiments intended to test the validity of Beer's law by using repetitive electron pulses at millisecond time intervals, it was necessary to use a different pulse source since the Febetron is not capable of a high repetition rate. For this purpose a Varian V-7715A linear accelerator, which is used in this laboratory³ for fast reaction studies in solution, provided a repetitive electron pulse. This accelerator is useful over the energy range 2–6 MV. The present work was done at about 3 MV. The pulse width may be varied from 1.5 μsec to about 5 nsec. In this work the pulse width used was between 0.2 and 1.5 μsec . The maximum current is approximately 350 mA. The repetition rate was about 300 pulses/sec. A 3-msec interval between pulses is sufficiently short, at the pressures used, so as not to drastically deplete the H-atom concentration by diffusion to the wall, an effect for which an accurate correction to the concentration may readily be made.

Detection System

The lamp for emission of the resonance line at 1215.7 Å was an electrodeless hydrogen discharge lamp, as described,¹ powered by a Raytheon Model PGM-10x2 microwave generator, and used an Evenson type resonant cavity. The lamp was designed with a short (3 mm) discharge region to minimize line reversal⁴ and

was operated at low pressure (3 torr) to avoid pressure broadening of the emission line.

Gaseous oxygen, which exhibits a transmission band⁵ at 1214–1220 Å, was used as an optical filter.¹ A correction of 4.5% to the optical density measurement was made to account for the amount of light extraneous to the Lyman- α line.

The detector, Model 641J-08-18 of Electro-Mechanical Research, Inc., was a vacuum-uv photomultiplier with a potassium bromide coated cathode. The characteristics of its response and operation have been described.¹

Reaction Cell

A stainless steel reaction cell¹ with lithium fluoride windows and an aluminum-mylar window for the electron beam was used for all the reaction studies. Cells of somewhat different size and geometry were used, depending largely on the optical absorption characteristics of the reactant gas.

The larger of the two cells, used for the reactions with oxygen and with carbon monoxide, had an optical path length of about 6.5 cm. The smaller cell, used with nitric oxide and with ethylene, had an optical path length of about 1.8 cm. Apart from the path length, the cells were of similar design.

Sample Preparation

Carbon monoxide, C. P. grade, obtained from J. T. Baker Chemical Co., was purified by two different methods. The impurity with which we were concerned is oxygen since the specific rate of reaction of H atoms with oxygen is more than two orders of magnitude higher than with carbon monoxide. The first purification method was the treatment of the carbon monoxide on a hot platinum wire catalyst at about 300°C, so that the reaction $\text{CO} + \frac{1}{2}\text{O}_2 = \text{CO}_2$, the equilibrium for which lies far to the right, would convert the trace oxygen to carbon dioxide. The carbon dioxide could then be condensed in liquid nitrogen. The second purification method used a sodium-potassium alloy (80% K, 20% Na) through which the carbon monoxide was bubbled to remove any trace of oxygen.

Nitric oxide, from J. T. Baker Chemical Co., was purified by vacuum distillation at 93°K to 77°K.

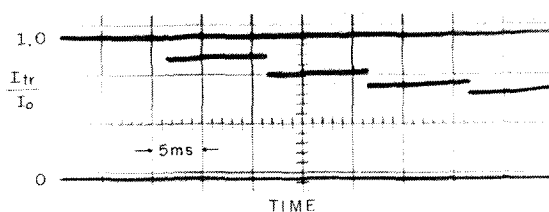


FIG. 1. Lyman- α absorption in hydrogen gas at 1550 torr following repetitive, reproducible electron pulses from linear accelerator.

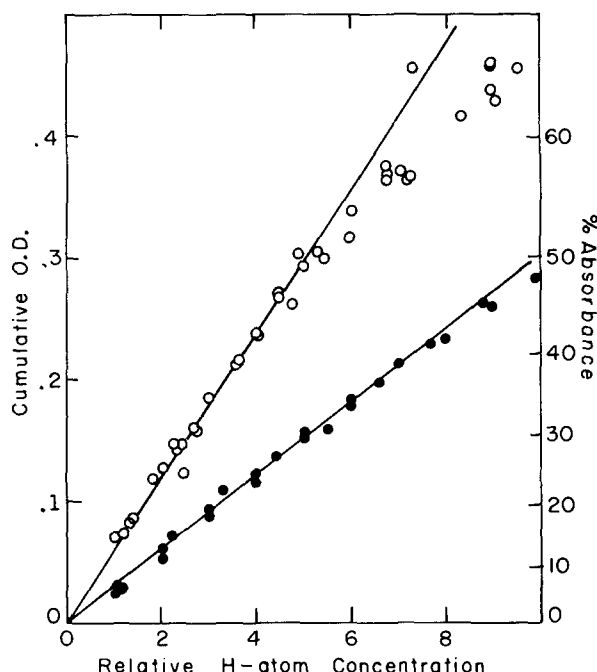


FIG. 2. Test of validity of Beer's law from repetitive pulse data. These sets of data are normalized for pulse intensity. The cumulative optical density, or percent absorbance, is shown for two pressures of hydrogen (O, 1550 torr; ●, 500 torr) as a function of relative H-atom concentration on an arbitrary scale.

Ethylene was deaerated by repeated trap-to-trap distillation at 77°K.

Argon, of ultrahigh purity grade, obtained from Matheson Co., was used in some runs without purification, in others after bubbling through a Na-K alloy. The observed lifetimes of hydrogen atoms with these different samples were identical.

Oxygen purified in the earlier work¹ was used. Matheson research grade hydrogen was purified¹ by passage through a Ag-Pd thimble.

RESULTS AND DISCUSSION

Validity of Beer's Law

The crux of the interpretation of the data from these fast reaction studies, utilizing the absorption of the resonance line for detection, lies in the validity of the application of Beer's law to these optical density data. It is appropriate, for a number of reasons, to question *a priori* the application of Beer's law in the absence of experimental justification. The oscillator strength for the $^2P_{3/2,1/2} \leftarrow ^2S_{1/2}$ transition in atomic hydrogen is very high,⁴ and the intrinsic linewidth small,⁶ so that a mismatch of the line profile in emission and absorption could result in a nonlinear relationship between the optical density and the H-atom concentration. Doppler broadening or line shift in emission, as well as line reversal in emission,⁶ would contribute to such an effect.

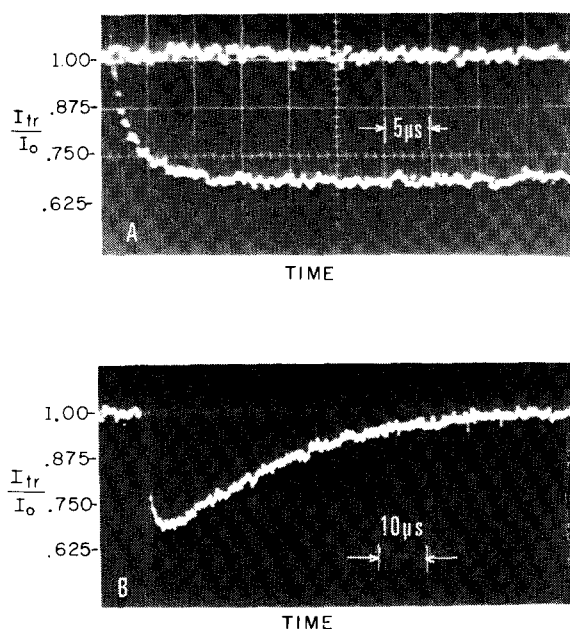


FIG. 3. (a) Rate curve for Lyman- α line showing electronic recovery of detection system following an electron pulse in hydrogen at 500 torr in the small cell. (b) Rate curve showing reaction of H atoms with nitric oxide at 2.31 torr in hydrogen gas at 504 torr.

Pressure broadening of the absorption line profile, on the other hand, would tend to nullify these effects so that it is advantageous, as has been pointed out,¹ to work at high pressures as in our system. Because of these considerations, experimental evidence was presented in our earlier report¹ which indicated that deviation from Beer's law is not serious in our system, even at relatively high absorption.

The matter is of sufficient importance to warrant the most direct experimental tests possible, and we have, accordingly, carried out additional experiments, using repetitive reproducible electron pulses from our linac to build up integral multiples of an initial H-atom concentration. The maximum pulse repetition rate is about 300 pulses/sec, and the pulse intensity is reproducible to about $\pm 3\%$. Since the disappearance of the H atoms by diffusion to the walls (and to a much lesser extent by recombination) occurs over many tens of milliseconds,¹ the atoms produced decayed only fractionally during the interval between pulses. A precise correction for the amount of this decay could be made from the known first-order decay rate in hydrogen. The concentration of H atoms produced per pulse could also be varied by changing the pulse length (0.2–1.5 μsec). A typical oscilloscope trace showing a stepwise increase in the absorption of the Lyman- α line produced by a set of 0.2 μsec pulses, at 10-msec intervals, in hydrogen gas at 1550 torr is shown in Fig. 1. Similar data were also obtained at lower pressure and at shorter intervals. From such data the relationship between the relative H-atom concentration (at fixed increments) and the

optical density could be examined in various optical density ranges.

Since the electronic recovery of the detection system is considerably longer (as evidenced by some upward curvature in the initial portion of the trace) with the linac than with the Febetron, the optical density was read at the end of each trace immediately before the next electron pulse. The corrected optical density at the beginning of each trace was then calculated using the measured first-order decay constant for atomic hydrogen. In Fig. 1 this correction ranges from 5% to 10%. Data obtained with several different pulse lengths and at two different hydrogen pressures are shown in Fig. 2. It is clear that Beer's law is completely valid to an optical density of at least 0.25 (40% absorption) so that no correction to the data is required throughout this range, over which most of the data are taken. Above about 50% absorption, derivation from Beer's law begins to be significant. No analytical expression for the extent of the deviation has been developed since kinetic data are generally not taken at optical densities exceeding 0.25, the most common range being 5% to 35% absorption.

Reaction with Nitric Oxide

The rate constant for Reaction (3), with molecular hydrogen as the third body, was determined at 25°C. Since the optical extinction coefficient⁷ of nitric oxide for the Lyman- α line is more than two orders of magnitude higher ($\epsilon_{\text{NO}}^{1216} \cong 60 \text{ atm}^{-1} \cdot \text{cm}^{-1}$) than for oxygen or carbon monoxide, it is necessary to use a cell with a somewhat shorter optical path to the photomultiplier tube. For this system, the smaller cell with an optical path length of 1.8 cm was used, which not only de-

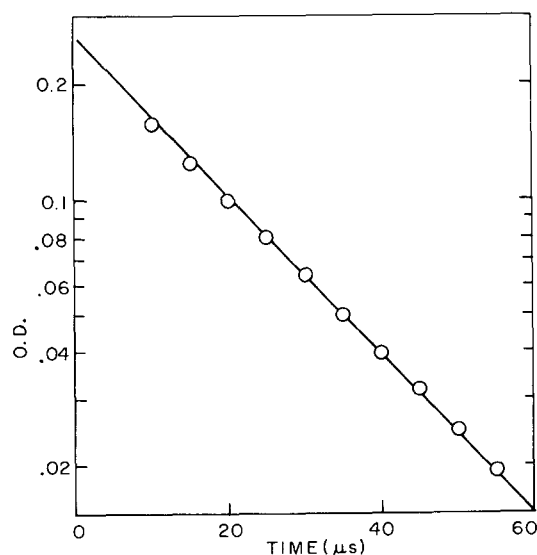


FIG. 4. First-order rate law plot of rate curve in Fig. 3(b) corrected for detector recovery. Log of the optical density is plotted against time.

creased the extent of absorption but also increased the absolute intensity because of the smaller distance. The fraction of NO photolyzed during a set of runs was very small since relatively high NO pressures were used. At NO pressures in excess of 0.5 torr, there was no change in the first-order decay constant for H atoms over a period of 30 min with the lamp on. Actual measurements for a given cell-filling required somewhat less than 5 min.

With this smaller cell, the time for electronic recovery of the detection system from the effects of the pulse, possibly because of higher X-ray intensity, was somewhat longer than for the larger cell,¹ amounting to about 10 μ sec. This may be seen in Fig. 3(a), which shows a rate curve observed in pure hydrogen at 500 torr. A good horizontal is attained after some 10–12 μ sec. A typical rate curve for Reaction (3), with H₂ as third body at 504 torr, and with 2.31 torr NO, is shown in Fig. 3(b). A small correction, based on the “formation” portion of Fig. 3(a), is applied to the initial portion (10–12 μ sec) of the rate curve in Fig. 3(b). With this correction, this rate curve is then found to fit very well to a first-order rate law, as may be seen from the straight line in Fig. 4, from the slope of which k_3 is determined. The correction for the recovery curve, although it helps to define the slope more precisely, has only a small effect on its magnitude. The correction function, which depends upon the hydrogen pressure and charging voltage (dose), was obtained for each set of experimental conditions.

With the concentration of NO constant at 2.3 torr, the pressure of H₂ was varied from 100 to 1500 torr to verify the third-body effect. Figure 5 shows the second-order rate constant as a function of hydrogen pressure. From the slope of the line the third-order rate constant, at 25°C, is found to be $k_3^{H_2} = (1.34 \pm 0.16) \times 10^{10} M^{-2} \cdot \text{sec}^{-1}$. Figure 6 shows the second-order rate constant as a function of NO pressure with H₂ pressure constant at 800 torr. The slope of this line gives $k_3^{H_2} = (1.40 \pm 0.12) \times$

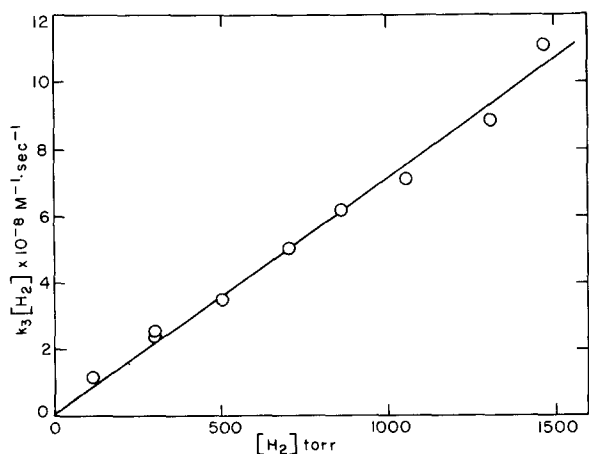


FIG. 5. Second-order rate constant $k_3[H_2]$ as a function of hydrogen pressure. The slope of the line gives $k_3^{H_2} = 1.34 \times 10^{10} M^{-2} \cdot \text{sec}^{-1}$.

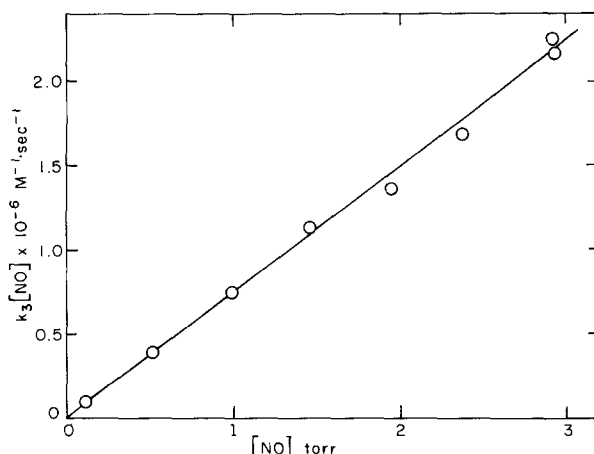


FIG. 6. Second-order rate constant $k_3[NO]$ as a function of NO pressure. The slope of the line gives $k_3^{H_2} = 1.40 \times 10^{10} M^{-2} \cdot \text{sec}^{-1}$.

$10^{10} M^{-2} \cdot \text{sec}^{-1}$. The data from all 17 experiments gives

$$k_3^{H_2} = (1.37 \pm 0.16) \times 10^{10} M^{-2} \cdot \text{sec}^{-1},$$

indicating a specific reaction rate with NO almost identical to that with oxygen.

Our value of $1.4 \times 10^{10} M^{-2} \cdot \text{sec}^{-1}$ for $k_3^{H_2}$ may be compared with several values in the recent literature, obtained by drastically different methods. There is excellent agreement with the value of Simionatis⁸ ($1.1 \times 10^{10} M^{-2} \cdot \text{sec}^{-1}$) obtained with an isothermal calorimeter as detector (applying a correction for the effect of the probe itself in the system) as there is with the more recent of two values of Clyne and Thrush⁹ ($1.48 \times 10^{10} M^{-2} \cdot \text{sec}^{-1}$) obtained by observation of the red emission from HNO*. The small disagreement with the recent value of Hartley and Thrush¹⁰ ($2.07 \times 10^{10} M^{-2} \cdot \text{sec}^{-1}$) is only slightly outside the limits of uncertainty. It would seem, therefore, that a value of $1.4 \times 10^{10} M^{-2} \cdot \text{sec}^{-1}$ or of one very close to that figure is now reasonably well established, having been obtained in flow systems as well as by fast reaction techniques.

Reaction with Oxygen

We had previously¹ determined the rate constant for Reaction (1) with H₂ as third body to be $k_1^{H_2} = 1.7 \times 10^{10} M^{-2} \cdot \text{sec}^{-1}$. In this investigation the rate constant was determined with argon as third body. Hydrogen was added, always at pressures very much lower than the argon and in some runs as low as 2 torr, to provide a source of hydrogen atoms. Rate curves were observed over a time range for which the half-time was on the order of 15–40 μ sec, so that any correction for the short, initial recovery curve¹ with the large cell was negligible.

The reaction was investigated over a range of oxygen pressure from 0.98 to 4.9 torr and argon pressure from 500 to 1130 torr. The decay of hydrogen atoms under all conditions was found to fit closely to a first-order rate

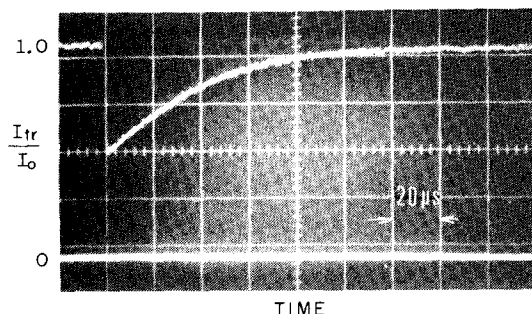


FIG. 7. Rate curve showing reaction of H atoms with oxygen at an oxygen pressure of 2.9 torr, argon 681 torr, and hydrogen 1.8 torr.

law. A typical rate curve is shown in Fig. 7. The results are summarized in Fig. 8, which shows the dependence of the second-order rate constant upon oxygen and upon argon. For oxygen ranging from 0.98 to 4.88 torr and argon constant at 796 torr, the data give $k_1^{\text{Ar}} = (5.75 \pm 0.68) \times 10^9 M^{-2} \cdot \text{sec}^{-1}$. For argon varying from 494 to 1130 torr and oxygen constant at 2.97 torr, the data give $k_1^{\text{Ar}} = (5.98 \pm 0.64) \times 10^9 M^{-2} \cdot \text{sec}^{-1}$. The effect of the small amount of hydrogen present has been taken into account in calculating these values. From the combined data, the value is

$$k_1^{\text{Ar}} = (5.87 \pm 0.68) \times 10^9 M^{-2} \cdot \text{sec}^{-1},$$

which is slightly lower than the values of Gutman *et al.*,¹¹ who have reported $8.6 \times 10^9 M^{-2} \cdot \text{sec}^{-1}$, and Clyne and Thrush,¹² who have reported $7.9 \times 10^9 M^{-2} \cdot \text{sec}^{-1}$, obtained by completely different methods. Dodonov *et al.*¹³ have reported a value of $2.2 \times 10^{10} M^{-2} \cdot \text{sec}^{-1}$ for this reaction with helium as third body, but no direct comparison can be made in the absence of reliable data on the relative efficiencies of helium, hydrogen, or argon. Taking our values for hydrogen and for argon as third body, we find the ratio of these third-body efficiencies to be $k_1^{\text{H}_2}/k_1^{\text{Ar}} = 2.9$.

Reaction with Carbon Monoxide

Since the rate constant for Reaction (2) is more than two orders of magnitude smaller than that of Reaction (1), it is important that traces of oxygen be removed from the carbon monoxide. The kinetic data to be presented include results obtained with both purification methods which have been described. Although relatively high concentrations of CO could be used in these experiments in view of the low molar extinction coefficient for the Lyman- α line, the rate of Reaction (2) was sufficiently slow under the experimental conditions to permit some concurrent disappearance of H atoms by diffusion to the wall



and to a negligible extent by recombination



A precise correction for the contribution of Reaction (5) to the decay of the H-atom signal was made from rate curves in pure hydrogen.¹ The amount of this correction was generally less than 10%.

Rate curves were observed for CO pressures from 0.3 to 8.9 torr, and hydrogen pressures from 210 to 1400 torr. All rate curves were found to fit closely to a first-order rate law with half-times typically on the order of 0.1 to 1 msec. From the slopes of these lines, the value of k_2 was determined after applying the correction for the occurrence of Reaction (5). Figure 9 shows a plot of the second-order rate constant for Reaction (2) as a function of CO pressure at a hydrogen pressure of 1220 torr, there being some normalization for hydrogen pressure. The slope of this line gives a third-order rate constant of $k_2^{\text{H}_2} = (3.93 \pm 0.68) \times 10^7 M^{-2} \cdot \text{sec}^{-1}$ at 298°K. Figure 10 shows a similar plot of the second-order rate constant $k_2[\text{H}_2]$ against pressure of hydrogen, with some normalization for CO concentration. The value of the rate constant obtained from the slope is $k_2^{\text{H}_2} = (4.01 \pm 0.60) \times 10^7 M^{-2} \cdot \text{sec}^{-1}$. Two points in Fig. 10 are the results of purification of CO with Na-K, while the remainder are for runs in which purification was done on the platinum wire. The absence of any discrepancy between the two sets lends some confidence regarding

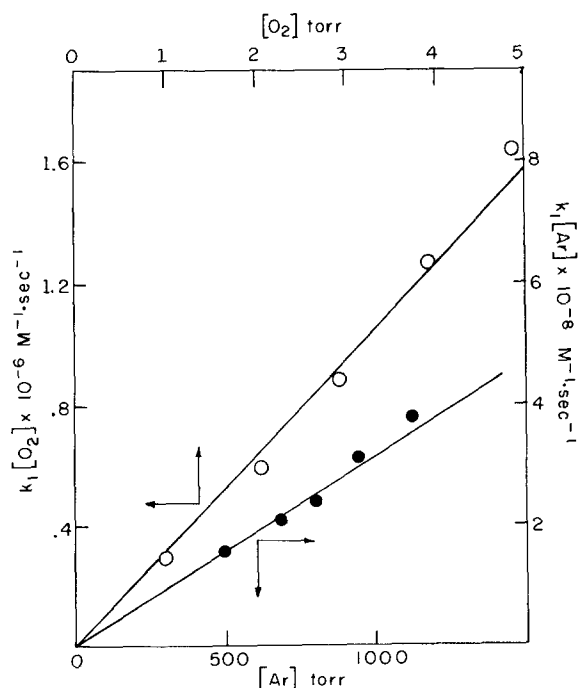


FIG. 8. Second-order rate constants $k_1[\text{O}_2]$ as a function of oxygen pressure (\circ) and $k_1[\text{Ar}]$ as a function of argon pressure (\bullet). The slopes of the lines give $k_1^{\text{Ar}} = 5.87 \times 10^9 M^{-2} \cdot \text{sec}^{-1}$.

the efficacy of the purification. Figure 11 shows the results of a series of runs in which a solution of 1220 torr H_2 and 0.98 torr CO was pulsed successively 13 times, with varying dose. The rate constant is plotted against the initial optical density. There is thus no trend in the value over a sixfold variation in the initial H-atom concentration (which is in the range of $5 \times 10^{-8} M$ or lower for this system as well as the others) or with the large number of pulses. All the data taken together give

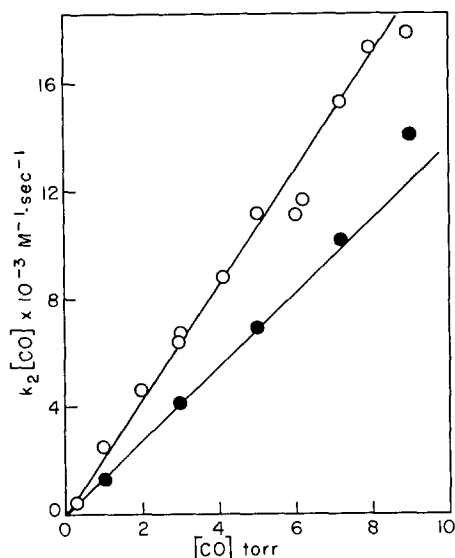


FIG. 9. Second-order rate constants $k_2[CO]$ as a function of CO pressure. (O, hydrogen 1220 torr; ●, argon 800 torr). The slopes of the lines give $k_2^{H_2} = 3.93 \times 10^7 M^{-2} \cdot \text{sec}^{-1}$ and $k_2^{Ar} = 2.63 \times 10^7 M^{-2} \cdot \text{sec}^{-1}$.

a value, with H_2 as third body, of

$$k_2^{H_2} = (3.97 \pm 0.64) \times 10^7 M^{-2} \cdot \text{sec}^{-1}.$$

A number of experiments were also done with argon as third body. In these runs a high argon pressure was used along with a low pressure of H_2 , sufficient to produce H atoms, and a pressure of CO appropriate to the desired kinetics. The correction for the concurrent diffusion of H atoms to the wall is applied as before. The results are presented in Figs. 9 and 10. In the former the CO pressure is varied from 1 to 5 torr with 800 torr argon; in the latter the argon pressure is varied from 600 to 1600 torr with 3 torr CO. Reasonably straight lines through the origin are obtained in each case, and from the slopes of these we obtain $k_2^{Ar} = (2.57 \pm 0.26) \times 10^7$ and $k_2^{Ar} = (2.63 \pm 0.44) \times 10^7 M^{-2} \cdot \text{sec}^{-1}$, respectively. Averaging all the data, we obtain, for Ar as third body,

$$k_2^{Ar} = (2.60 \pm 0.36) \times 10^7 M^{-2} \cdot \text{sec}^{-1}.$$

The ratio of the efficiencies of hydrogen and argon as

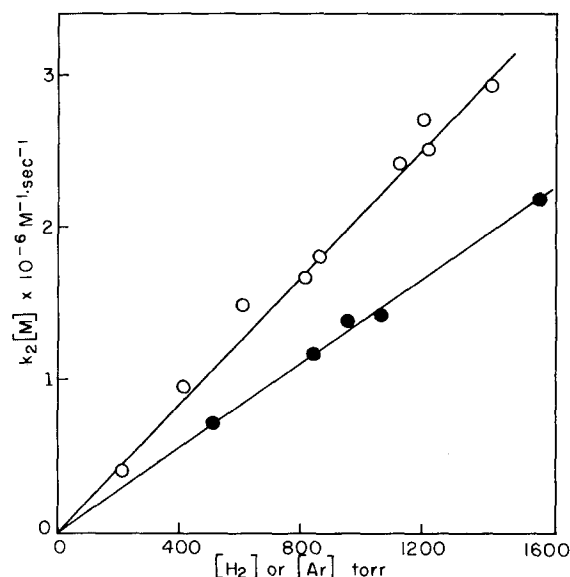


FIG. 10. Second-order rate constants $k_2[M]$ [$M = H_2$ (O), $M = Ar$ (●)] as a function of the pressure of M. The slopes of the lines give $k_2^{H_2} = 4.01 \times 10^7 M^{-2} \cdot \text{sec}^{-1}$ and $k_2^{Ar} = 2.57 \times 10^7 M^{-2} \cdot \text{sec}^{-1}$.

third body in Reaction (2) is thus $k_2^{H_2}/k_2^{Ar} = 1.5$, somewhat lower than the analogous ratio for the reaction of H atoms with oxygen.

Reaction with Ethylene

Determination of the rate constant for Reaction (4) is complicated in the region of low to moderate pressures (1 to 75 torr) by redissociation of the vibrationally excited ethyl radical:



which, at sufficiently high pressures, may be fully

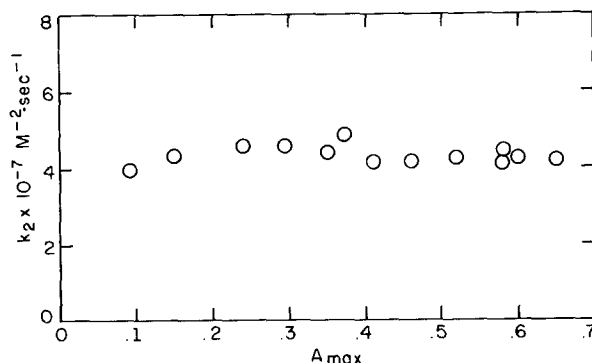


FIG. 11. Third-order rate constant $k_2^{H_2}$ as a function of the initial optical density. Hydrogen pressure = 1215 torr, CO pressure = 0.98 torr.

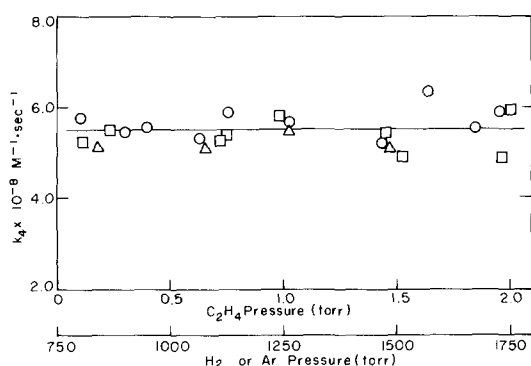
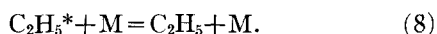


FIG. 12. Rate constant for $\text{H} + \text{C}_2\text{H}_4$ as a function of pressure of C_2H_4 (\square with $\text{H}_2 = 800$ torr), of H_2 (\circ with $\text{C}_2\text{H}_4 = 1.0$ torr), and of Ar (Δ with $\text{H}_2 = 100$ torr and $\text{C}_2\text{H}_4 = 1.0$ torr).

collisionally deactivated:



As a result, all recent attempts¹⁴⁻¹⁹ to define k_4 reliably from the apparent rate constant in the pressure dependent region, have involved extrapolation of varying extent to the high pressure limit. Since the fast reaction method we are using is applicable at relatively high pressure, it appeared feasible to determine k_4 at pressures sufficiently high for Reaction (8) to occur rapidly and for which constancy in the value of k_4 could be demonstrated, thus settling any controversy concerning the magnitude of the rate constant which, of necessity, serves as a benchmark for many studies of Reaction (7).

Runs were done with H_2 as third body, and in a few cases with Ar as third body, over a pressure range of 750 to 1750 torr, 10- to 25-fold higher than the highest pressures used previously. Ethylene pressure ranged from 0.1 to 2.0 torr. A typical rate curve and a first-order plot were shown in our preliminary report² of the results. Figure 12 shows the data obtained over the total range of pressures of H_2 , of Ar, and of C_2H_4 . Initial $[\text{H}]$, not shown, was varied tenfold. Good constancy is obtained in this high-pressure region, giving

$$k_4 = (5.5 \pm 0.5) \times 10^8 \text{ M}^{-1} \cdot \text{sec}^{-1} \text{ at } 298^\circ \text{K}.$$

The same result is obtained with both H_2 and Ar as third body, which should be the case in the high-pressure limit.

This value is higher than that reported by Westenberg and de Haas,¹⁷ whose ESR data require a very long extrapolation from 2.5 torr, and by Barker *et al.*¹⁹ The value is in excellent agreement with the recent value of 6.0×10^8 reported by Braun and Lenzi¹⁴ at 75 torr and not in very serious disagreement with a value of

8.2×10^8 , which has been currently obtained²⁰ in the same laboratory.

The disagreement with the ESR data is to be explained by the long extrapolation required to high pressures. On close inspection, the data of these authors¹⁷ shows some curvature which had not been taken into account and which has now been clearly demonstrated by Kurylo *et al.*²⁰ The disagreement with the value of Barker *et al.*¹⁹ may simply reflect a complication inherent in their method. Because of the longer times in their photolytic method, they are unavoidably involved with a stoichiometry correction. From our result and the recent¹⁴ and current result²⁰ from Braun's group, it appears that the higher values are reliable.

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