PHYSICAL REVIEW VOLUME 114, NUMBER 1 APRIL 1, 1959

Attachment of Low-Energy Electrons in Mixtures Containing Oxygen

G. S. HURST* AND T. E. BORTNER
Health Physics Division, Oak Ridge National Laboratory, Oak Ridge, Tennessee

(Received October 27, 1958)

Electron attachment to O_2 has been studied for O_2-N_2 and $O_2-C_2H_4$ mixtures over a wide range of pressures and electric fields. It was found that α, the probability of capture per cm and per mm Hg of O_2, depends on the partial pressures of both gases in the O_2-N_2 mixture but only on the C_2H_4 pressure in the $O_2-C_2H_4$ mixture. The data have been interpreted in terms of an extension of the mechanism postulated by Bloch and Bradbury, and by Bates and Massey, which involves first the formation of O_2^{-*} (excited O_2^-) with subsequent collisional stabilization. On this basis estimates were made of the cross section for stabilization of O_2^{-*} by collisions with various kinds of molecules.

I. INTRODUCTION

THE mechanism by which electrons are attached to O_2 appears to depend critically on the energy of the electrons. At thermal energy the magnitude of the capture cross section is so low (10^{-22} cm^2) that the mechanism may be the direct formation of O_2^- which is stabilized by radiation.[1]

At slightly higher energies the cross section increases to such a value (10^{-20} cm^2) that stabilization by radiation can no longer be offered as a reasonable mechanism. Bradbury,[2] Doehring,[3] and Chanin and Biondi[4] have shown that starting at approximately 0.4 ev, the capture cross section decreases with energy up to 1.2 ev. Bloch and Bradbury[5] have postulated that in this energy range the mechanism involves the formation of $O_2^{-\prime}$ (i.e., virbationally excited O_2^-) which is subsequently stabilized by collision. Based on the experimental observation by Bradbury[2] that the cross section for attachment was independent of O_2 pressure even as low as 3.5 mm Hg, Bloch and Bradbury[5] reasoned that the cross section for stabilization of $O_2^{-\prime}$ by O_2 would have to be about 100 times the gas-kinetic cross section. Bates and Massey[6] and Massey and Burhop[7] have pointed out that the magnitude of this cross section is difficult to understand, particularly in view of the fact that calculations by Zener[8] have shown that even in the case of exact resonance, a similar[9] energy transfer cross section must be much smaller than gas-kinetic.

Many observers[10–13] have studied the capture of electrons in oxygen at still higher electron energies and several other mechanisms have been postulated for these energies. However, very little additional data have been obtained which add to our understanding of the low-energy process (i.e., in the energy range between thermal energy and 1.2 ev). A study of the attachment process in O_2 for electrons in this energy range is the subject of this report.

II. METHOD

Suppose an α particle forms n_0 electrons at a distance d from a positively charged electrode. Because of attachment, at a distance x from the point of formation, only n of the electrons are free (i.e., not attached). The number dn attached in a distance dx is given by

$$dn = -\alpha n f_1 P dx, \qquad (1)$$

which defines α, the probability of attachment per cm of travel in the field direction and per mm of partial pressure (f_1P) of the attaching gas. Let $P = f_1P + f_2P$, where f_1P is the partial pressure of the attaching gas and f_2P is the partial pressure of a nonattaching gas. In this work, $f_1P \ll f_2P$; thus E/P refers approximately to the "reduced electric field"—volts per cm and per mm Hg of the nonattaching gas.

The time variation of the electrostatic potential of a plane electrode ionization chamber, due to the motion of electrons in the uniform field, depends on the electron drift velocity and the attachment coefficient α. Suppose the resulting pulse is examined with a pulse amplifier having a step function response,

$$V'(t) = (t/t_1)e^{-t/t_1}, \qquad (2)$$

where t_1 is the "time constant" of the amplifier. If t_1 is chosen to be comparable to the collection time, τ_0, for free electrons in the chamber and is much less than the time of collection of negative ions, then the maximum pulse height, $V(\tau')$, is a simple function of

---

* This material will be submitted by G. S. Hurst as a part of a dissertation for the degree of Doctor of Philosophy at the University of Tennessee.

[1] M. A. Biondi, Phys. Rev. **84**, 1072 (1951).

[2] N. E. Bradbury, Phys. Rev. **44**, 883 (1933).

[3] A. Doehring, Z. Naturforsch. **7a**, 253 (1952).

[4] L. M. Chanin and M. A. Biondi, Westinghouse Research Laboratories Research Report 6-94439-7-R5, October 1, 1957 (unpublished).

[5] F. Bloch and N. Bradbury, Phys. Rev. **48**, 689 (1935).

[6] D. R. Bates and H. S. W. Massey, Trans. Roy. Soc. (London) **A239**, 269 (1943).

[7] H. S. W. Massey and E. H. S. Burhop, *Electronic and Ionic Impact Phenomena* (Clarendon Press, Oxford, 1952), pp. 262 and 474.

[8] C. Zener, Phys. Rev. **37**, 556 (1931).

[9] Transfer of vibrational energy from the first excited level in N_2 to a normal N_2 molecule at room temperature.

[10] M. A. Harrison and R. Geballe, Phys. Rev. **91**, 1 (1953).

[11] D. S. Burch and R. Geballe, Phys. Rev. **106**, 183 (1957).

[12] Craggs, Thorburn, and Tozer, Proc. Roy. Soc. (London) **A240**, 473 (1957).

[13] H. D. Hagstrum, Revs. Modern Phys. **23**, 185 (1951).

t_1 and τ_0. Figure 1 shows the results of the evaluation of the expression for various values of τ_0/t_1 as a function of $f=\alpha fPd$.

In one section of a plane electrode ionization chamber[14] the pulse height due to the motion of electrons, produced by alpha-particle ionization, is measured. The drift velocity of electrons is measured in another part of the same ionization chamber. These two measurements furnish data from which the attachment coefficient is calculated. The method is convenient for studies where it is desirable to use very small amounts of O_2 in larger amounts of nonattaching gases. This approach permits one to study the attachment to O_2 over a wide range of mean electron energy by proper choice of the nonattaching gas,[15] and to investigate the behavior of the attachment process in O_2 in the presence of other kinds of molecules.

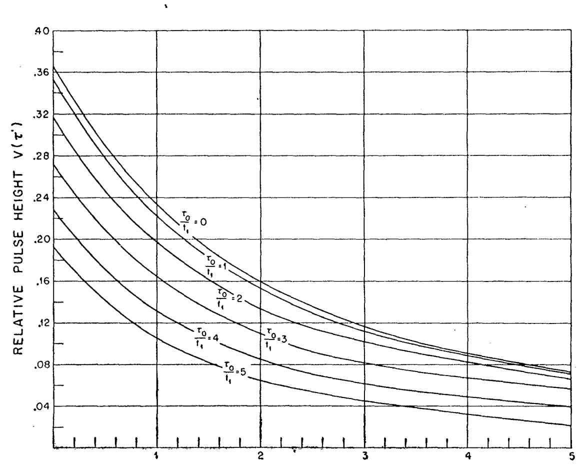

FIG. 1. Calculated dependence of pulse height on f for various values of τ_0/t_1.

III. MIXTURES OF OXYGEN AND NITROGEN

Data for drift velocity in nitrogen have been reported,[16] where it was found that (a) as much as 2% did not affect the measured drift velocity, and (b) the drift velocity of the electrons in the mixtures was a function of E/P but independent of total pressure P. Pulse-height data were taken for various pressures of nitrogen and oxygen as a function of E/P; a typical set is shown in Fig. 2. Data were also obtained for N_2 pressures 600, 800, 1000, 1200, 1400, and 1600 mm Hg, and the same range of O_2 pressure (1–8 mm Hg).

Calculated results for α show dependence on the O_2 pressure, f_1P, as well as the N_2 pressure, f_2P. Figure 3 shows the results for $E/P=0.40$. The analysis for α was performed at other values of E/P yielding the same general type of dependence on f_1P and f_2P. The results are described by the empirical equation

$$\alpha=Af_1P+Bf_2P+Cf_1Pf_2P, \tag{3}$$

where A, B, and C are independent of f_1P and f_2P, but depend on E/P as shown in Table I. In Fig. 3 the solid lines are calculated from Eq. (3), adjusted to fit the experimental data points. This is the first case where it is found that the cross section for the formation of stable O_2^- definitely depends on pressure. Bradbury's[2] experiment failed to show the dependence of α on oxygen pressure, even with pressure as low as 3.5 mm Hg. It is worth noting, however, that only a meager amount of data were reported for values of E/P less than 2. Earlier work of Cravath[17] did, in fact, indicate a dependence of attachment cross section on oxygen pressure, which was more pronounced at low values of E/P.

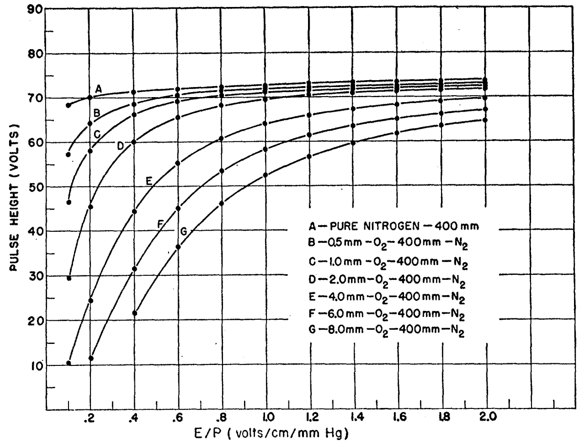

FIG. 2. Pulse height *vs* E/P for mixtures of O_2 and N_2.

Because of the complexity of the result obtained for α, data were taken for two different source-to-plate separations, d. The values for α were the same for the

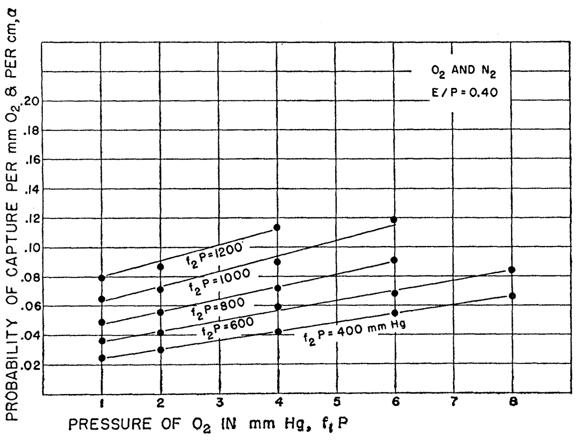

FIG. 3. Attachment coefficient α as a function of O_2 pressure for various N_2 pressures at $E/P=0.40$.

---

[14] A complete description of the method and apparatus is given in T. E. Bortner and G. S. Hurst, Health Phys. 1, 39 (1958).

[15] A convenient tabulation of mean agitation energy for various gases as a function of E/P may be found in R. H. Healey and J. W. Reed, *The Behavior of Slow Electrons in Gases* (The Wireless Press for Amalgamated Wireless Ltd., Sidney, Australia, 1941).

[16] Bortner, Hurst, and Stone, Rev. Sci. Instr. **28**, 103 (1957).

[17] A. M. Cravath, Phys. Rev. **33**, 605 (1929).

TABLE I. Empirical constants A, B, and C as a function of E/P for electron attachment in O_2-N_2 mixtures.

E/P	A	σ_1 (cm^2)	B	$\sigma_{2\,\max}$ (cm^2)	C
0.2	4.5×10^{-3}	2.1×10^{-15}	1.4×10^{-4}	6.4×10^{-17}	2.2×10^{-5}
0.4	2.4×10^{-3}	3.0×10^{-15}	5.3×10^{-5}	6.8×10^{-17}	7.6×10^{-6}
0.6	1.5×10^{-3}	3.1×10^{-15}	2.9×10^{-5}	5.9×10^{-17}	2.4×10^{-6}
0.8	1.3×10^{-3}	3.2×10^{-15}	1.8×10^{-5}	4.4×10^{-17}	9.0×10^{-7}

normal separation of 6.0-cm and a 9.0-cm separation. This rules out the possibility of a nonuniform rate of attachment. Such an effect could arise for example, because of the finite distance required for the electrons created by the α particles to slow down to the equilibrium energy distribution characterized by the E/P and the nature of the gas.

To understand the pressure dependence of α, we will attempt to develop a model for the formation of stable O_2^-, which follows to some extend the original ideas of Bloch and Bradbury. The first step is assumed to be the formation of unstable O_2^{-*} according to the reaction

$$\text{(a)} \qquad O_2+e^- \rightarrow O_2^{-*},$$

or the direct formation of stable O_2^- by the process

$$\text{(b)} \qquad O_2+e^-+X \rightarrow O_2^-+X^T,$$

where X is the nonattaching member of the binary mixture and T designates a transfer of energy. The asterisk indicates that the O_2^- ion has enough excited energy (either electronic or vibrational) to make the reverse of process (a) possible. The absence of the asterisk does not mean that O_2^- is in its ground state, but merely that the ion is energetically stable. A reaction like (b) but where another O_2 replaces X would not be of importance since in general $f_1P \ll f_2P$. We further postulate that O_2^{-*} may be stabilized by the reactions

$$\begin{array}{ll}
\text{(c)} & O_2^{-*} \rightarrow O_2^- + h\nu, \\
\text{(d)} & O_2^{-*}+O_2 \rightarrow O_2^-+O_2^T, \\
\text{(e)} & O_2^{-*}+X \rightarrow O_2^-+X^T, \\
\text{(f)} & O_2^{-*}+O_2+X \rightarrow O_2^-+O_2^T+X^T,
\end{array}$$

or the electron may be spontaneously emitted by the reaction

$$\text{(g)} \qquad O_2^{-*} \rightarrow O_2+e^-.$$

The number of electrons, dn_a, which react to form O_2^{-*} [process (a)] while n electrons are moving a distance dx in the field direction is given by

$$dn_a = -\beta n f_1 P dx, \tag{4}$$

where β is a constant. The number of electrons dn_b attached by process (b) is given similarly by

$$dn_b = -k n f_1 P f_2 P dx, \tag{5}$$

where k is a constant. On the other hand, the coefficient of attachment α is defined by Eq. (1). Clearly then, $dn = f_s dn_a + dn_b$, where f_s is the fraction of the number of O_2^{-*} which are stabilized. Thus,

$$\alpha = f_s\beta + k f_2 P, \tag{6}$$

where the fraction f_s is determined by processes (c) through (g).

Defining the rates for processes (c), (d), (e), (f), and (g) by

$$(dN/dt)_c = -\lambda_1 N, \quad (dN/dt)_d = -C_1 N f_1 P,$$
$$(dN/dt)_e = -C_2 N f_2 P, \quad (dN/dt)_f = -K N f_1 P f_2 P, \tag{7}$$

and

$$(dN/dt)_g = -\lambda_2 N,$$

leads to f_s such that

$$\alpha = \left(\frac{\lambda_1 + C_1 f_1 P + C_2 f_2 P + K f_1 P f_2 P}{\lambda_1 + C_1 f_1 P + C_2 f_2 P + K f_1 P f_2 P + \lambda_2}\right)\beta + k f_2 P. \tag{8}$$

Equation (8) reduces to the form required for the O_2-N_2 case (Eq. 3) if λ_1 is assumed to be negligible in the numerator of the first term and if $\lambda_2 \gg \lambda_1 + C_1 f_1 P + C_2 f_2 P + K f_1 P f_2 P$. Then,

$$\alpha = \frac{C_1}{\lambda_2}\beta f_1 P + \left(\frac{C_2\beta}{\lambda_2} + k\right) f_2 P + \frac{K}{\lambda_2}\beta f_1 P f_2 P, \tag{9}$$

which is the form required by the experimental data, Eq. (3). The condition that λ_1 be small is reasonable, since Biondi[1] has shown that only at thermal energies can an appreciable part of the attachment cross section be attributed to radiation stabilization. The condition that λ_2 be larger than the pressure-dependent terms in the denominator of Eq. (8) would hold only at "low" pressures. The values of the empirical constants A, B, and C, Table I, may now be equated to $C_1\beta/\lambda_2$, $(C_2\beta/\lambda_2 + k)$, and $K\beta/\lambda_2$, respectively.

In order to calculate the cross sections corresponding to the rate constants, we must determine β/λ_2. This will be done directly from the Bloch-Bradbury paper, although the principle of detailed balance could be used. Thus,

$$\beta/\lambda_2 = \text{constant} \times f(E^*)/v_0(E^*)^{\frac{1}{2}}, \tag{10}$$

where $f(E^*)$ is the energy distribution function evaluated at the particular electron energy E^* at which the electron is captured by O_2, and v_0 is the mean agitation velocity of the electron. The cross-section estimates[18] shown in Table I are based on the Bloch-Bradbury values for E^* and $f(E^*)$. Thus, the cross section, σ_1 for process (d) is approximately 3×10^{-15}

---

[18] In relating the rate constant C_1 to cross section σ_1, we used the convention of A. C. G. Mitchell and M. W. Zemansky, *Resonant Radiation and Excited Atoms* (Cambridge University Press, London, 1934), p. 155. Other conventions [e.g., R. D. Present, *Kinetic Theory of Gases* (McGraw-Hill Book Company, Inc., New York, 1958), p. 153] would lead to cross sections which are Π times those reported in Table I.

cm^2, and the maximum value of the cross section, $(\sigma_2)_{\max}$ for process (*e*), for the N_2-O_2 case, is approximately 6×10^{-17} cm^2.

Uncertainties in the potential energy diagram of O_2^- prohibit detailed interpretation of processes (*d*) and (*e*). In the Bloch-Bradbury work it was assumed that the excited energy of the O_2^{-*} ion was vibration only; thus, in this picture σ_1 would represent the cross section for the transfer of vibrational energy from O_2^{-*} to O_2. Theoretical arguments[8,19] are against vibrational transfer cross sections of this magnitude, even when the polarization effect[20] is included. Bates and Massey[6] argue that the electron affinity of O_2 is about 1 ev and point out the possibility that the O_2^{-*} ion may be in an $O_2^{-\prime}(^4\Sigma_u^-)$ state; i.e., vibration (designated by the prime) of O_2^- in its $(^4\Sigma_u^-)$ electronic state.[21] In this case the cross section σ_1 may represent the sum of two distinct processes: (1) transfer of vibrational energy, and (2) transfer of electronic excitational energy by the reaction

$$O_2^{-\prime}(^4\Sigma_u^-)+O_2(^3\Sigma_g^-)\rightarrow O_2^{-\prime}(^2\Pi_g)+O_2(^1\Delta_g).$$

This process may take place with large probability since the energy balance is almost exact if the $(^4\Sigma_u^-)$ energy level of Bates and Massey is adopted.†

Regardless of the potential energy curves of O_2^-, it is likely that process (*e*) is simply the transfer of vibration from O_2^{-*} to N_2, since in N_2 the first excited electronic level lies more than 5 ev above its ground state. Thus, the suggestion that O_2^{-*} is initially in an $O_2^{-\prime}(^4\Sigma_u^-)$ state is very attractive in view of our findings that the ratio $\sigma_1/\sigma_{2\,\max}$ is $\gg1$.

In Table I it is seen that the cross section σ_1 is nearly independent of *E*/*P* (and hence the electron agitation energy) as, of course, it should be if we are dealing with the same excited states in O_2^{-*}. The fact that σ_1 is not entirely independent of *E*/*P* can easily be explained by our lack of knowledge of *f*(*E*) and *E**. The fact that $\sigma_{2\,\max}$, obtained by neglecting process (*b*), does depend on *E*/*P* may be taken as evidence that *k*, representing the rate constant for process (b), is not negligible in the O_2-N_2 mixtures.

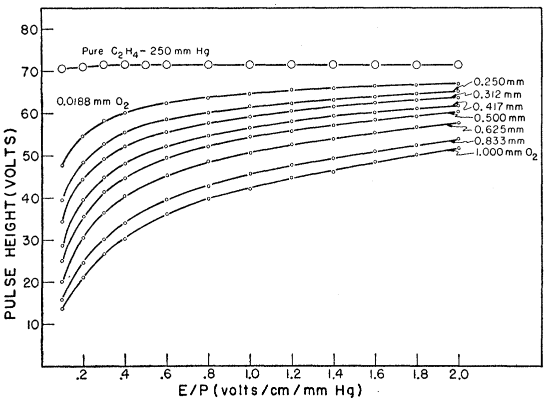

FIG. 4. Pulse height *vs* *E*/*P* for mixtures of O_2 and C_2H_4. (0.0188 in figure should read 0.188).

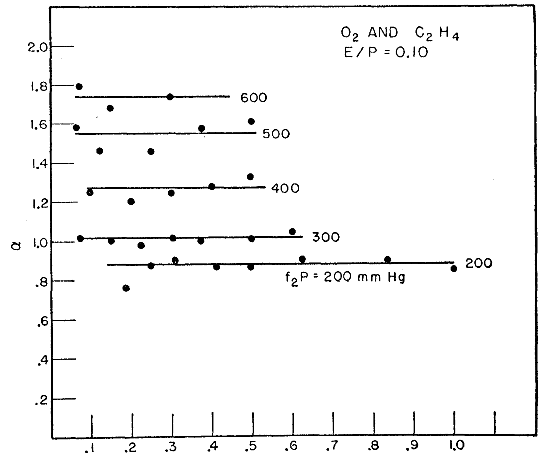

FIG. 5. Attachment coefficient α as a function of O_2 pressure for various C_2H_4 pressures at $E/P=0.10$.

The most surprising result of fitting the above model of electron capture to the experimental data for N_2-O_2 is the large value of the constant *K* representing the rate process (*f*). The usual kinetic-theory criterion for three-body collisions[22] fails completely. A possible reason may be that O_2^{-*} and N_2 combine to form $(O_2^{-*}-N_2)$ with a mean life against molecular dissociation which is much longer than the electron emission time.‡

IV. ATTACHMENT OF ELECTRONS IN ETHYLENE-OXYGEN MIXTURES

An investigation, similar to the one conducted for O_2-N_2 mixtures, was carried out for $O_2-C_2H_4$ mixtures. Drift-velocity data have already been

---

[19] O. K. Rice, Phys. Rev. **38**, 1943 (1931).

[20] E. Vogt and G. H. Wannier, Phys. Rev. **95**, 1190 (1954).

[21] See L. M. Branscomb, in *Advances in Electronics and Electron Physics*, edited by L. Marton (Academic Press, Inc., New York, 1957), Vol. 9, p. 61, for revised potential energy curves for O_2^-.

† Strictly speaking, β/λ_2 as given in Eq. (10) should be multiplied by a factor of 2 if evaluated for the $^4\Sigma_u^-$ state, making the cross sections σ_1 and $(\sigma_2)_{\max}$ a factor of 2 smaller than those reported in Table I.

[22] R. C. Tolman, *Statistical Mechanics with Application to Physics and Chemistry* (Chemical Catalog Company, Inc., New York, 1927), p. 243 ff.

‡ *Note added in proof.*—Equating the experimentally determined rate of stabilization to the rate of triple collisions, with the assumption that the electron emission time λ_2^{-1} is much less than the time against molecular dissociation, leads to an estimate of λ_2^{-1}. When the cross sections for the processes $O_2^{-*}+N_2\rightarrow(O_2^{-*}-N_2)$ and $(O_2^{-*}-N_2)+O_2\rightarrow O_2^-+N_2+O_2^*$ are both set equal to 10^{-14} cm^2, the value of λ_2^{-1} is approximately 5×10^{-11} sec compared to the Bloch-Bradbury estimate of 10^{-10} sec. The assumption that the ion-molecule "sticky time" is $\gg\lambda_2^{-1}$ is quite reasonable since an estimate of the "sticky time" for $O_2^{-*}-N_2$, following the statistical mechanics approach [H. Eyring, J. Chem. Phys. **3**, 107 (1935); J. L. Magee, Proc. Nat'l. Acad. Sci. **38**, 764 (1952); M. Burton and J. L. Magee, J. Phys. Chem. **56**, 842 (1952)], is 5×10^{-9} sec for a binding energy of 0.2 ev and 6 internal degrees of freedom.

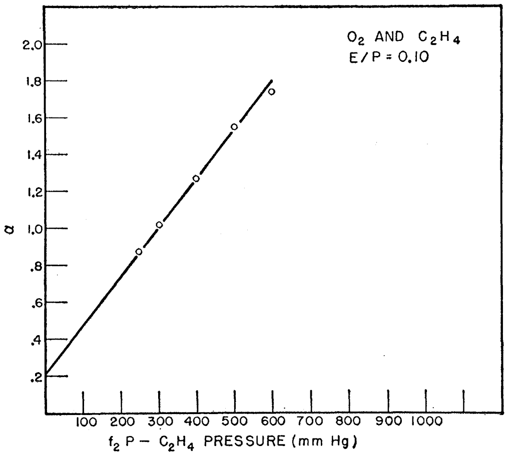

FIG. 6. Attachment coefficient α as a function of C_2H_4 pressure.

reported.[16] A sample of pulse-height data for total ethylene pressure of 250 mm Hg is shown in Fig. 4. Similar data were taken for C_2H_4 pressures 300, 400, 500 and 600 mm Hg.

A sample set of values for α is shown in Fig. 5 for $E/P=0.10$; similar sets were calculated for E/P values 0.20, 0.30, 0.40, 0.50, 0.60, 0.80, 1.0, 1.2, 1.4, 1.6, 1.8, and 2.0. In all cases α was independent of the 0_2 pressure f_1P, but did depend on the C_2H_4 pressure. Figure 6 is a plot of α as a function of ethylene pressure, f_2P, for $E/P=0.10$. At all values of E/P the curve of α against f_2P is a straight line, which has a positive intercept for $f_2P=0$. All the data can be represented with the simple empirical equation

$$\alpha=\alpha_0+k'f_2P, \tag{11}$$

where α_0 and k' are independent of pressures f_1P and f_2P but do depend on E/P, Fig. 7.

Although the dependence of α on f_1P and f_2P for the case of $O_2-C_2H_4$ is rather different from the case of O_2-N_2 it is possible to retain the model which was postulated for the O_2-N_2 case. Assume that all the reactions (a) through (g) hold for $O_2-C_2H_4$ mixtures; i.e., let a C_2H_4 molecule replaces the X molecules in every process. The attachment coefficient, α, given in Eq. (8), reduces to the form required by experiment, Eq. (11), with either of two conditions: (a) $\lambda_1 \gg C_1f_1P+C_2f_2P+Kf_1Pf_2P$, or (b) $\lambda_2+\lambda_1 \ll C_1f_1P+C_2f_2P+Kf_1Pf_2P$. For condition (a),

$$\alpha=[\lambda_1/(\lambda_1+\lambda_2)]\beta+kf_2P; \tag{12a}$$

while condition (b) gives

$$\alpha=\beta+kf_2P. \tag{12b}$$

We have shown in connection with the O_2-N_2 data that $\lambda_1/(\lambda_1+\lambda_2)\ll 1$; thus if condition (a) holds, α_0 [in Eq. (11)] would have to be less than β by a large factor. On the other hand, if condition (b) holds, α_0 would be of the same order as β. When Bradbury's value of h, the probability of capture per collision, is extrapolated to an electron energy of 0.08 ev (corresponding to $E/P=1.2$ in C_2H_4)[15] and used to obtain α, we find $\alpha=4\times10^{-3}$ as compared to $\alpha_0=4\times10^{-2}$ at $E/P=1.2$. Thus β as determined from the Bradbury data is smaller than α_0 by a factor of 10, and one can conclude that condition (*b*) holds and the value of α, as determined from extrapolating Bradbury's results, is a factor of 10 smaller than β. Condition (b) will, of course, not hold at low values of f_1P and f_2P, but appears to hold over the entire pressure range covered by the present experiment (f_1P ranged from 0.19 to 1.0 mm Hg and f_2P ranged from 250 to 600 mm Hg).

We then set $\alpha_0=\beta$ and $k'=k$, where β and k are defined in Eqs. (4) and (5), respectively. The magnitude of k is not difficult to justify even on the basis of the kinetic theory of gases for three-body reactions.[22] If one uses the approach of Tolman, it is found that the rate constant k is no larger than the rate of three-body collisions, even when gas-kinetic cross sections are used for all types of collisions involved.

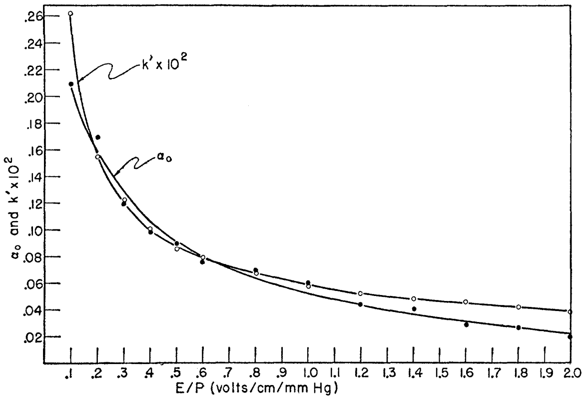

FIG. 7. Empirical constants α_0 and $k'\times10^2$ as a function of E/P for $O_2-C_2H_4$ mixtures.

ACKNOWLEDGMENTS

The authors are pleased to acknowledge the comments and criticisms of Professor R. D. Present (University of Tennessee), Professor A. H. Nielsen (University of Tennessee), Professor R. L. Platzman (Purdue University), and Professor Milton Burton (University of Notre Dame). We are also indebted to R. H. Ritchie, J. A. Harter, H. F. Holzer, and R. H. Jones of Oak Ridge National Laboratory for their continuing contributions to this work.