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The Reaction of Hg($^3P_1$) with Ethylene†

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The reaction of Hg($^3P_1$) with ethylene at room temperature has been re-investigated. Special attention was paid to the effects of the concentrations of ethylene and mercury on the reaction velocity. The results are in general agreement with a mechanism which requires the excited ethylene, produced initially, to decompose both in the gas phase and on the wall. The results are also compatible with the suggestion that a significant fraction of the quenching collisions between ethylene and Hg($^3P_1$) leads to the formation of metastable ($^3P_0$) atoms.

INTRODUCTION

THERE have been several previous investigations of the reactions of Hg($^3P_1$) atoms with ethylene. The most recent of these was by LeRoy and Steacie,[1] who postulated that an excited ethylene molecule was produced in the initial act and that this could either decompose homogeneously or be deactivated by collision with an unexcited ethylene molecule. They also suggested that some C_4 hydrocarbons might have been formed at high pressures, since under those conditions the partial pressure of acetylene was no longer the same as the total pressure increase. This mechanism requires the reciprocal of the rate of hydrogen production to be a linear function of the concentration of ethylene when the concentration of ethylene is high enough for quenching to be complete. However, as mentioned in a previous communication,[2] the results of LeRoy and Steacie do not agree with their mechanism but appear to obey the relationship

$$I/R=A+Bp^2.$$

The present investigation was undertaken to study more carefully the effect of pressure and of the concentration of mercury on the rate of production of hydrogen, and also to examine the reactions responsible for the suggested formation of the C_4 hydrocarbons.

EXPERIMENTAL

The reaction system consisted of a cylindrical quartz cell, with plane quartz windows, connected via a quartz-Pyrex graded seal to a McLeod gauge and a mercury cutoff. The apparatus was evacuated and filled through the mercury cutoff which was also used as a manometer. The quartz cell (10 cm×5-cm diam) was placed vertically and connected to the rest of the system near the bottom face. A low pressure mercury lamp with neon (3 mm) as a carrier gas was used as a source of unreversed λ2537. The radiation from the lamp was approximately collimated by a quartz lens and defined by a 2.5-cm stop. A drop of mercury in the bottom of the cell provided a constant and controllable concentration of mercury in the reaction volume. The lower 2 cm of the cell was surrounded by a large Dewar flask, which was used as a thermostat to control the concentration of mercury in the vapor phase. Water was used as the thermostat fluid, and the level was adjusted so that the top of the horizontal portion of the tube connecting the reaction flask to the rest of the system was always well covered by the liquid. Agitation of the thermostatic liquid by a slow stream of air ensured a constant temperature throughout the bath. The total volume of the system was 440 cc to which the reaction cell contributed 196 cc.

The reaction was followed by freezing out the unreacted ethylene and any condensable products with liquid nitrogen, and measuring the pressure of the permanent gas with the McLeod gauge. LeRoy and Steacie[1] have shown that hydrogen is the only detectable substance that is not removed at the temperature of liquid nitrogen. They have also shown that the rate of pressure increase decreases with continued illumination, and they ascribed this to increased quenching by hydrogen. Accordingly, in the present investigation the reaction was followed over very small conversions, the maximum pressure of hydrogen being less than 5×10^{-2} mm, so that complications due to quenching by hydrogen should not have been significant. This was confirmed by preliminary experiments which established (a) that the pressure of hydrogen was, within the accuracy of the measurements, a linear function of time, (b) that there was no detectable change in the transparency of the incident window due to the deposition of polymer, and (c) that successive experiments could be carried out using the same sample of ethylene, without flaming the cell, with no detectable change in rate because of the accumulation of condensable products.

The intensity of λ2537 was estimated by using the mercury photosensitized decomposition of propane as an actinometer. The rate of production of hydrogen from propane (440 mm) was measured, and when 0.48 was used for the quantum efficiency,[3] the intensity was estimated to be 2.9×10^{-7} einstein min^{-1}. This value was the average of several determinations, among which the

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[1] D. J. LeRoy and E. W. R. Steacie, J. Chem. Phys. **9**, 829 (1941).

[2] B. deB. Darwent, J. Chem. Phys. **19**, 258 (1951).

[3] S. Bywater and E. W. R. Steacie, J. Chem. Phys. **19**, 319 (1951).

TABLE I. The effect of pressure on the quantum yield.

intensity ≈ 2×10^{-7} einstein min^{-1}; beam diameter = 2.5 cm
volume of system = 440 cc; Hg saturator = 20.0°C

Expt. No.	Pressure mm Hg	Rate—mm $\text{min}^{-1}\times10^3$ Observed	Standard	ϕ_{H_2}
54	9.80	3.27_5	2.78	0.380
41	13.3_5	3.02	2.76	0.351
52	29.0	2.37_5	2.83	0.270
40	30.3	2.24	2.76	0.260
44	38.1	1.95	2.72	0.230
50	45.0	1.79	2.83	0.203
46	45.4	1.73	2.81	0.198
51	55.0	1.51	2.83	0.172
43	56.0	1.38_5	2.72	0.164
47	66.0	1.21_5	2.81	0.139
49	66.0	1.25	2.83	0.142
61	73.5	1.07	2.64	0.130
58	82.0	0.97_6	2.76_5	0.113
62	86.1	0.93	2.64	0.113
57	91.8	0.87	2.76_5	0.101
63	96.0	0.80	2.64	0.097
56	99.5	0.76	2.76_5	0.089

variation was less than ±5 percent. Experiments were carried out with ethylene and propane alternately, the temperature of the mercury supply being 20.0±0.1°C. The following values were obtained for the quantum yield of the hydrogen production from ethylene at various pressures:

Pressure of C_2H_4 mm	ϕ_{H_2}
10.65	0.375
39.8	0.222
48.5	0.186

The value of 0.375 for ϕ_{H_2} at 10.65 mm may be compared with that of 0.37 for 13 mm of ethylene, found by LeRoy and Steacie, who used uranyl oxalate as the actinometer.

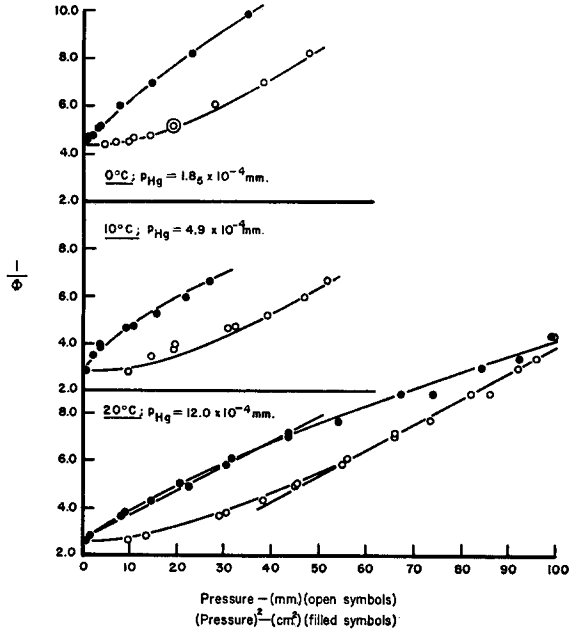

FIG. 1. The effect of ethylene pressure on the quantum yield. Mercury saturator temperature: top—0.0°C; middle—10.0°C; bottom—20.0°C.

Some difficulty was experienced in maintaining the light intensity constant over prolonged intervals, and this made the comparison of rates obtained several days apart somewhat uncertain. Hence the intensity was checked each day by carrying out experiments under standard conditions and referring all results to the standard rates obtained on that day. In practice, at least, two standard runs were made on each day, and the results showed that between these two runs the intensity remained constant. The standard conditions were 19.2±0.2 mm with the mercury supply at 20.0 ±0.1°C, and by interpolation of the results given above for ϕ_{H_2} at various pressures the value of ϕ under standard conditions (ϕ_s) was found to be 0.321.

RESULTS

The effect of pressure on the quantum yield with the mercury supply at 20.0°C is shown by the data given in Table I. The standard rates ($R_{H_2}{}^s$) used for calculating the quantum yields at the various pressures are given in column 4. These are the average results of two experiments done immediately before and after the experiments to which they are applied. The individual determinations of $R_{H_2}{}^s$ did not differ from the average by more than ±2 percent and were usually much closer to the average than ±1 percent. The reciprocal quantum yields are shown as a function of pressure (p) and (p^2) in Fig. 1. It is evident from Fig. 1 that neither the p nor p^2 plot is linear and that they deviate from linearity in opposite directions. In the experiments at high mercury concentration (20°C), the plot of $1/\phi_{H_2}$ against p^2 appears to be linear at low pressures (up to about 40 mm) and to intersect the $1/\phi$ axis at about the point 2.65. The fact that the p and p^2 curves deviate from linearity in opposite directions suggests that $1/\phi$ is actually a composite function of p and p^2. This is consistent with $C_2H_4{}^*$ decomposing in the gas phase as well as on the wall.

TABLE II. Effect of mercury concentration on the quantum yield.

Pressure of C_2H_4 = 19.2(±0.1) mm

Saturator (°C)	P_{Hg} mm $\times10^4$	ϕ_{H_2}
20.0	12.0	0.321
0.0	1.8_5	0.197
16.0	8.5	0.297
10.0	4.9	0.266
4.0	2.8	0.230
23.5	16.1	0.335

Further indication that decomposition of $C_2H_4{}^*$ on the wall plays a significant part in the over-all process is provided by the effect of mercury pressure on ϕ_{H_2}. These results (Table II) show that the quantum yield decreases progressively with decreasing concentration of mercury vapor. By plotting ϕ against $\log p_{\mathrm{Hg}}$ (Fig. 2) it becomes evident that the results are in good agreement with a linear relation between those two parameters. The linear relationship between ϕ and $\log p_{\mathrm{Hg}}$ may be explained by assuming that the absorption of λ2537 by mercury was incomplete, since the amount of light absorbed is an exponential function of the concentration of mercury, so that a linear relationship exists between the absorbed intensity and $\log p_{\mathrm{Hg}}$. However, calculations based on a reasonable value of the absorption coefficient[4] of mercury for λ2537, and independent experiments‡ both showed that the λ2537 should be almost completely absorbed in a 10-cm path even at the lowest concentration of mercury used. It may therefore be concluded that the decrease in rate with decreasing concentration of mercury was due to some factor other than the decrease in absorbed intensity.

The effect of pressure on the quantum yield of hydrogen production with the mercury supply at 10.0°C and 0.0°C are given in Table III, which is analogous to Table I. The reciprocal quantum yields are plotted against p(mm) and p^2(cm²) in Fig. 1, and again we find that both plots deviate from straight lines.

In addition to the decomposition of $C_2H_4^*$, the nature of the deactivation was investigated. A pressure of 196 mm of ethylene was taken into the reaction system (McLeod gauge excluded) and exposed to λ2537 for 6.0 hours with the mercury supply at 0°C. The hydrogen produced amounted to 14.4×10^{-2} mm in the entire system. The condensable products were analyzed on the mass spectrometer and special attention was paid to the presence of C_4 hydrocarbons. No trace of C_4 hydrocarbons was found, indicating an upper limit of 0.03 percent C_4 in the condensable products.

Now at 0°C the initial quantum yield of hydrogen production, obtained by extrapolating to zero pressure, was 0.233. The intensity was about 2.0×10^{-7} einstein min⁻¹, so that there should have been $2.0\times10^{-7}\times6\times60\times0.233=16.8\times10^{-6}$ mole of $C_2H_4^*$ produced in 6 hours. The hydrogen actually produced amounted to 3.5×10^{-6} mole so that 13.8×10^{-6} mole of $C_2H_4^*$ were deactivated. The total condensable products was 3.36×10^{-3} mole, of which less than 0.03 percent were C_4 hydrocarbons. Hence, less than 1.01×10^{-6} mole of C_4 hydrocarbons were produced by the deactivation of 13.8×10^{-6} mole of $C_2H_4^*$. Each deactivating collision involves one excited and one normal ethylene molecule and, if C_4 hydrocarbons were produced in the "deactivation" step, one mole of C_4 should be produced for each $C_2H_4^*$ that is deactivated. Hence, the result of this experiment shows that less than 8 percent of the deactivating collisions at room temperatures lead to the production of C_4 hydrocarbons.

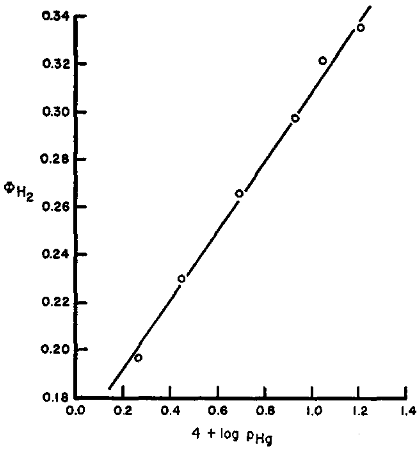

FIG. 2. The effect of mercury concentration on the quantum yield. Ethylene pressure—19.2 mm Hg.

DISCUSSION

The following reactions,

$$C_2H_4+Hg(^3P_1)\rightarrow C_2H_4^*+Hg(^1S_0) \qquad (1)$$

$$C_2H_4^*+C_2H_4\rightarrow 2C_2H_4 \qquad (2)$$

$$C_2H_4^*\rightarrow C_2H_4+H_2, \qquad (3)$$

were suggested[1] as a mechanism that would account for the nature of the products and for the effect of pressure on the rate of the mercury photosensitized reaction of ethylene. From this mechanism the relationship

$$1/R_3=\frac{1}{k_1[^3P_1]}\cdot\frac{1}{[C_2H_4]}+\frac{k_2}{k_1k_3[^3P_1]} \qquad (A)$$

was derived, and it was concluded that "a plot of $1/R_3$ *vs* $1/C_2H_4$ should give a straight line for which the ratio of the intercept on the $1/R_3$ axis to the slope is k_2/k_3." By assuming a reasonable value for k_2, τ_3 (or $1/k_3$), the average life of the excited ethylene molecule, was found to be about 10^{-7} sec. In a previous com-

TABLE III. Effect of pressure on the quantum yield at low mercury concentration. Conditions as in Table I except for mercury concentration.

Hg saturator—10°C			Hg saturator—0°C		
Pressure mm	Rate mm min⁻¹×10³	ϕ_{H_2}	Pressure mm	Rate mm min⁻¹×10³	ϕ_{H_2}
19.1_5	2.11	0.266	27.9	1.33	0.166
9.8_5	2.88	0.362	9.9_5	1.77	0.220
14.4_5	2.28	0.287	14.2_5	1.70	0.212
33.0	1.67	0.210	4.78	1.82_5	0.227
18.9_5	1.82	0.254	6.98	1.79	0.223
30.6	1.69	0.216	2.54	1.76	0.219
51.6	1.18	0.151	18.9	1.56	0.194
39.0	1.49	0.191	18.8	1.56_5	0.194
46.9	1.31_5	0.168	38.3	1.14	0.143
			47.9	0.97	0.122
			59.0	0.807	0.101
			10.6_5	1.69	0.213

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[4] A. C. G. Mitchell and M. W. Zemansky, *Resonance Radiation and Excited Atoms* (Cambridge University Press, Cambridge, 1934).

‡ It was found that at least 96 percent of λ2537 was absorbed in a distance of 15 mm by mercury at a pressure of 20×10^{-4} mm in the presence of 100 mm of hydrogen.

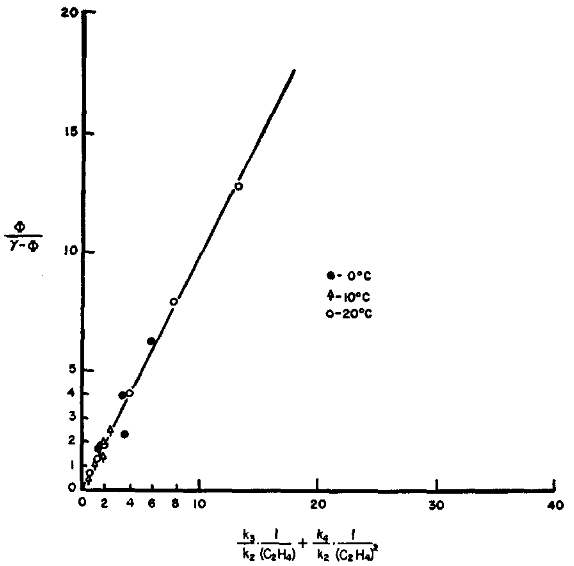

FIG. 3. The effect of the concentrations of mercury and ethylene on the quantum yield.

munication[2] it was pointed out that the foregoing mechanism does not agree with experiment and that the derivation of τ_3 from Eq. (A) is not valid. We shall discuss this mechanism in the light of data obtained in the present investigation, the value of τ_3, and the deactivation of excited ethylene.

Mechanism of the Reaction

In any discussion about the mechanism of the mercury photosensitized reaction of ethylene, the processes

$$Hg(^1S_0)+h\nu \rightarrow Hg(^3P_1), \qquad (a)$$

$$Hg(^3P_1) \rightarrow Hg(^1S_0)+h\nu \qquad (b)$$

must, obviously, be considered in addition to reactions (1), (2), and (3). The usual stationary state treatment yields the following result:

$$[^3P_1]=I_a/(k_b+k_1[C_2H_4]). \qquad (B)$$

This may be introduced into Eq. (A) to give

$$1/\phi=1+(k_2/k_3)[C_2H_4], \qquad (C)$$

where $\phi=R_3/I_a$ is the quantum yield of the production of hydrogen. Hence, if the mechanism consisting of reactions (1), (2), and (3) is correct, the reciprocal quantum yield should be a linear function of the pressure, and the limiting extrapolated value at zero pressure should be unity. That such a relationship does not represent the experimental facts is obvious from Fig. 1. The results of LeRoy and Steacie[1] yield a straight line when $1/\phi$ is plotted against $[C_2H_4]^2$. For such a relationship to be valid it is necessary for the excited ethylene molecules to decompose on the wall,

$$C_2H_4^* \xrightarrow{\text{wall}} C_2H_2+H_2, \qquad (4)$$

rather than homogeneously [as by reaction (3)], or for the deactivation process to occur only as the result of a triple collision,

$$C_2H_4^*+2C_2H_4 \rightarrow 3C_2H_4. \qquad (5)$$

This latter process (5) appears to be most improbable and could hardly be reconciled with relatively low quantum yields since these require an efficient deactivation process. If we assume that the heterogeneous process (4) is responsible for the decomposition, we obtain, by the usual stationary state treatment, the relationship

$$1/\phi=1+(k_2/k_4)[C_2H_4]^2, \qquad (C')$$

which agrees with the results of LeRoy and Steacie and, even if over only a limited range of conditions, with the results of the present experiments. Some support for reaction (4) is provided by the effect of mercury concentration on ϕ at constant pressure of ethylene (Fig. 2), which shows that ϕ decreases logarithmically with the concentration of mercury. This is understandable since k_4 must be assumed to be some function of the distance through which the excited ethylene molecules diffuse before they attain the wall, which is itself a logarithmic function of the concentration of mercury.

TABLE IV. Effect of mercury concentration on initial efficiency and rate constants.

Saturator (0°C)	(Dimensions are mole, liter) γ	$(k_3/k_2)\times10^3$	$(k_4/k_2)\times10^6$
20.0	0.400	1.04	3.27
10.0	0.333	1.15	2.63
0.0	0.233	2.46	2.55

That neither Eq. (C) or (C′) accurately describes the effect of concentration of ethylene on the quantum yield is obvious from the results plotted in Fig. 1. Since the plots deviate in opposite directions from the predicted straight lines we may conclude that processes (3) and (4) both occur and that their relative importance depends on the conditions of the experiment. This conclusion is supported by the fact that at high pressure the diffusion of excited ethylene molecules could become so slow that the average time taken for them to attain a wall would exceed their natural life.

If both reactions (3) and (4) are included, the following relationship is obtained:

$$\frac{\phi}{1-\phi}=\frac{k_3}{k_2}\cdot\frac{1}{[C_2H_4]}+\frac{k_4}{k_2}\cdot\frac{1}{[C_2H_4]^2}.$$

If we allow for the possibility of inefficiency in the initial act or in reaction (4), the above relationship may be shown to become

$$\frac{\phi}{\gamma-\phi}=\frac{k_3}{k_2}\cdot\frac{1}{[C_2H_4]}+\frac{k_4}{k_2}\cdot\frac{1}{[C_2H_4]^2}, \qquad (D)$$

where γ represents the product of the efficiencies of reactions (1) and (4). The value of γ may be obtained by extrapolation to zero concentration of the $1/\phi$ *vs* $[C_2H_4]$ or $1/\phi$ *vs* $[C_2H_4]^2$ curves in Fig. 1. By using the value of γ so obtained the best values of k_3/k_2 and k_4/k_2 (Table IV) were calculated by the method of least squares. The fact that $\phi/(\gamma-\phi)$ is a linear function of $1/[C_2H_4]+1/[C_2H_4]^2$, as demanded by Eq. (D), is shown in Fig. 3. Thus, the results are in reasonable agreement with the mechanism involving both the homogeneous and the heterogeneous decomposition of excited ethylene. The influence of the concentrations of ethylene and of mercury on the fraction of excited ethylene that decomposes on the wall is shown in Fig. 4. The fraction of the heterogeneous decomposition is given by the expression

$$\frac{(k_4/k_2)(1/[C_2H_4])^2}{(k_4/k_2)(1/[C_2H_4]^2)+(k_3/k_2)(1/[C_2H_4])}.$$

Although effects of changes in the concentrations of mercury and ethylene do indeed influence the rate of the reaction in the manner predicted by the mechanism, there are other effects which are not immediately predictable. These are as follows: (a) The value of γ is seen (Table IV) to decrease with decreasing mercury concentration whereas the suggested mechanism does not predict that there should be any change. (b) The ratios k_3/k_2 and k_4/k_2 appear to be functions of the concentration of mercury vapor. (c) The results given in Tables I and III seem to indicate that the maximum rate occurs at progressively decreasing pressures as the mercury concentration is decreased. (d) No plausible explanation has been given for the fact[1] that the maximum rate is obtained only when the pressure of ethylene is as high as 9–10 mm when the pressure of mercury is $1\text{-}2\times10^{-3}$ mm.

Quenching measurements indicate that reaction (b) should be negligible at pressures higher than about 2 mm, and so it may be expected that the maximum rate would occur at about 1 or 2 mm. Some results obtained recently[5] in these laboratories suggest that at least part of the quenching of λ2537 by ethylene occurs by virtue of the reaction

$$C_2H_4+Hg(^3P_1)\rightarrow C_2H_4'+Hg(^3P_0), \qquad (c)$$

where C_2H_4' represents ethylene with only a small amount (0.218 ev) of energy in excess of the thermal value. There are two reactions by which the metastable ($^3P_0$) atoms can disappear:

deactivation to the ground state by collision with ethylene,

$$C_2H_4+Hg(^3P_0)\rightarrow C_2H_4{}^*+Hg(^1S_0); \qquad (d)$$

or by collision with the wall,

$$Hg(^3P_0)\xrightarrow{\text{wall}}Hg(^1S_0)+E. \qquad (e)$$

There is no quantitative information about reaction (d), but Samson[6] found that with nitrogen the effective cross section for the transition $^3P_1\rightarrow{}^1S_0$ was very much greater than for $^3P_0\rightarrow{}^1S_0$. If a similar relationship holds for quenching by ethylene, it is obvious that deactivation of the metastable mercury atoms to the ground state by collision with ethylene may be complete only at a fairly high pressure. Hence without attempting a quantitative treatment of the problem, it is obvious that, if a significant fraction of the quenching occurs by the transition $^3P_1\rightarrow{}^3P_0$, the maximum rate may be reached at a pressure that is very much higher than that expected from the known quenching cross section. Also the maximum rate will occur when the rate of reaction (d) is small compared with that of (c). Since the rate of reaction (e) depends on the average distance through which the ($^3P_0$) atoms diffuse before they strike the wall it is not difficult to see, qualitatively, that the maximum rate of reaction will occur at smaller pressures as the distance of diffusion is increased (i.e., as the concentration of mercury is decreased). Thus the foregoing points (c) and (d) may be explained reasonably on the basis of quenching to the metastable state. An explanation along similar lines could be suggested for the influence of mercury concentration on γ and for the effect of [Hg] on k_4/k_2. However, the effect of concentration of mercury on the ratio k_3/k_2 appears to be quite inexplicable by a mechanism consisting of the reactions suggested above.

Average Life of Excited Ethylene

The average life of the excited ethylene produced in reaction (1) was calculated[1] to be about 10^{-7} sec. The value of k_2/k_3 was derived from the ratio of intercept to slope of the straight line that resulted when $1/R_3$ was

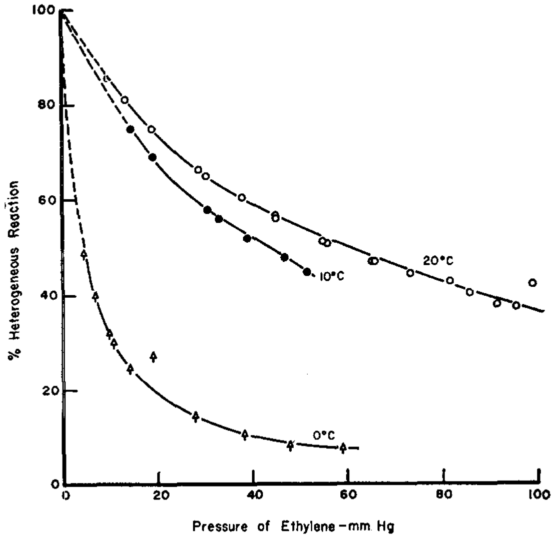

FIG. 4. The calculated effect of the concentrations of mercury and ethylene on the contribution of the wall reaction.

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[5] B. deB. Darwent and F. G. Hurtubise, J. Chem. Phys. **20**, 1684 (1952).

[6] E. W. Samson, Phys. Rev. **40**, 940 (1932).

plotted against $1/C_2H_4$ according to Eq. (A), and $1/k_3(=\tau_3)$ was obtained from this by using an assumed value for k_2. This procedure is not necessarily valid since, in general, the slope of the line is given by

$$\frac{d(1/R_3)}{d(1/C_2H_4)}=\frac{1}{k_1}\cdot\frac{1}{[^3P_1]}+\frac{1}{k_1}\cdot\frac{1}{[C_2H_4]}\cdot\frac{d(1/[^3P_1])}{d(1/[C_2H_4])}+\frac{k_2}{k_1k_3}\cdot\frac{d(1/[^3P_1])}{d(1/[C_2H_4])},$$

and it is only when $[^3P_1]$ is not a function of $[C_2H_4]$, i.e., when $d(1/[^3P_1])/d(1/[C_2H_4])=0$, that the slope will be equal to $1/k_1[^3P_1]$. The foregoing discussion has shown clearly that $[^3P_1]$ is, in fact, a function of $[C_2H_4]$, given by Eq. (B), and therefore the value of τ_3 as calculated by LeRoy and Steacie is not necessarily correct. The usual stationary state treatment applied to reactions (a), (b), (1), (2), (3), and (4) gives the equation

$$1/\phi=\left(\frac{k_b}{k_1[C_2H_4]}+1\right)\left(1+\frac{k_2[C_2H_4]^2}{k_3[C_2H_4]+k_4}\right). \quad \text{(E)}$$

At low pressures the term $(k_2[C_2H_4]^2)/(k_3[C_2H_4]+k_4)$ may be neglected compared with unity, and the simple relationship

$$1/\phi=(k_b/k_1[C_2H_4])+1$$

is obtained. If allowance is made for possible inefficiency in the initial act, the equation then becomes

$$1/\phi=(k_b/k_1[C_2H_4])+\gamma. \quad \text{(E}')$$

It is now obvious why a straight line was obtained when $1/\phi$ (or $1/k_3$) was plotted against $1/[C_2H_4]$. However, it is evident that the ratio of intercept to slope of this line does not bear any relationship to the average life of excited ethylene but is related to the quenching process.

Some values of k_3/k_2 from which the magnitude of $\tau_3(=1/k_3)$ may be obtained are listed in Table IV. The values of k_3/k_2 appear to be between 1 and 2×10^{-3} mole liter^{-1}. Taking an average value of 1.5×10^{-3} mole liter^{-1} for k_3/k_2 and assuming a value§ of 13×10^{10} liter mole^{-1} sec^{-1} for k_2, we get $k_3=2\times10^8$ sec^{-1} or $\tau_3=0.5\times10^{-8}$ sec. This value is quite different from those suggested earlier,[1,2] and it must be admitted that no great reliance should be placed on any of these estimates. The value given by LeRoy and Steacie[1] has been shown to have been based on a wrong premise. The value suggested in the author's previous note[3] was based on the assumption that no homogeneous decomposition occurs, and this is obviously wrong. The value calculated from k_3/k_2 may be considerably in error, since this ratio appears to be influenced by the concentration of mercury. However, if the trend (Table IV) of increasing value of k_3/k_2 with decreasing [Hg] is regarded as fictitious, the average life suggested above (0.5×10^{-8} sec) may have some validity, always provided that the assumptions about k_2 are correct.

Nature of the Deactivating Reaction

An interesting result obtained in this investigation is the very small yield of C_4 hydrocarbons at high pressures, which allows an upper limit of about 10 percent to be placed on the percentage of "deactivating" collisions that lead to the formations of C_4 hydrocarbons. This result is interesting since Laidler[7] suggested that the excited ethylene produced in the initial step is actually a vibrationally excited triplet, which may be expected to undergo reactions similar to those of other free radicals. It is well known that methyl radicals are capable of adding to the double bond of ethylene, and therefore, it may be expected that the triplet ethylene (biradical), with its vibrational excitation, would add rather easily. The results of this investigation show quite clearly that the reaction is not fast and that at least 90 percent of the collisions between excited ethylene and ethylene, in which the excited molecules are deactivated, lead only to deactivation and not to addition.

LeRoy and Steacie[8] also investigated the effect of temperature on the mercury photosensitized reactions of ethylene. They found that the rate of hydrogen production was not affected significantly by changes in temperature, but that at high temperatures a rapid, free-radical, sensitized polymerization of ethylene occurred. They therefore suggested that the reaction

$$Hg(^3P_1)+C_2H_4\rightarrow C_2H_3+H+Hg \quad (1')$$

occurred, as well as reaction (1). The free radical sensitized polymerization may then take place by virtue of processes of the type

$$C_2H_3+C_2H_4\rightarrow C_4H_7,$$
$$H+C_2H_4\rightarrow C_2H_5.$$

However, their results appear to be equally well explained by the assumption of only a single initial step (1) if we then have competition between the deactivation reaction (2) and a reaction of the type

$$\cdot CH_2-CH_2\cdot+C_2H_4\rightarrow\cdot CH_2-CH_2-C_2H_4$$

between excited ethylene and ethylene. The foregoing addition probably requires some energy of activation, which is unlikely with the deactivation reaction (2). This suggestion is, of necessity, purely speculative, since there is little information available about reactions of this type.

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§ Assuming that reaction (2) occurs on every collision.

[7] K. J. Laidler, J. Chem. Phys. 10, 43 (1942).

[8] D. J. LeRoy and E. W. R. Steacie, J. Chem. Phys. 10, 676 (1942).