



Mechanism of the Hg (3 P 1) Photosensitized Decomposition of Ethylene

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gaseous states (quantum mechanical calculations should apply to gaseous ions) despite the fact that it is such an extremely large difference.

If either the value of $\alpha(H^{-})$ of 14.6×10^{-24} cm³ calculated by Henrich⁵ or the value of 10.2×10⁻²⁴ cm³ given by Pauling⁴ is used in the calculation of the dipole moments of the gaseous alkali metal hydrides, negative dipole moments result. This situation arises from $a^3(\alpha_1+\alpha_2)+4\alpha_1\alpha_2 > a^6-4\alpha_1\alpha_2$ and also in most of the calculations from $\alpha_1 + \alpha_2 > a^3$. Such negative values for the dipole moments are physically impossible and must result from an incorrect assumption being made at some point in the calculations.

Since Pauling's values⁴ have been applied satisfactorily in numerous computations involving the need for the polarizabilities of gaseous ions, the value given for H⁻ should also be applicable. It is true that the possibility exists that the quantum mechanical calculations are grossly incorrect. In view of the fact that a variety of approximation methods give results which are in fair agreement with each other, this seems highly unlikely. Furthermore, the same functions when employed in calculating the polarizability of He give results which are in quite good agreement with each other and with the experimental value.¹⁰ This leaves the possibility that the classical electrostatic model used fails when it is applied to the alkali metal hydrides. This alternative is quite possibly the one responsible for the results obtained.

Rittner² has given an argument based on a model of a diatomic molecule consisting of a point charge +e at a distance a from a metal sphere of charge -e of radius R when $\alpha_1 \ll \alpha_2$, and has applied the method of images. This model is satisfactory for the alkali halides. The model is not satisfactory for the alkali metal hydrides because the condition that a > R is not satisfied. If a $R(H^{-})$ of 2.08A is accepted⁹ then the condition is not satisfied for LiH and NaH. If an $\alpha(H^-) = 14.6 \times 10^{-24} \text{ cm}^3$ is employed in the expression $R = \alpha^{\frac{1}{2}}$, then $R(H^{-}) = 244A$ and the condition is not satisfied by LiH, NaH, KH, or RbH, and is just barely satisfied by CsH. It seems likely then that the electrostatic model used^{1,2} fails for the alkali metal hydrides because of actual interpenetration of the large hydride ion by the alkali metal ion.

The reasonable agreement between the calculated and experimental binding energies is quite likely fortuitous. If an $\alpha(H^-)$ =14.6 \times 10⁻²⁴ cm³ is now employed in the calculation of the contribution to the binding energy made by the electrostatic terms, in the case of KH an increase of about 109 Kcal/mole is found over that obtained employing $1.80 \times 10^{-24} \, \mathrm{cm^3}$ for the $\alpha(\mathrm{H^-}).$ Furthermore, since the value of the compressibility ρ is dependent on the assumed model and the corresponding expression for the binding energy, use of a poor model resulting in an incorrect expression for the binding energy would also result in an incorrect compressibility and repulsive energy. Owing to this interdependence, a nearly correct binding energy might result from a cancellation of errors.



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Mechanism of the Hg $({}^{3}P_{1})$ Photosensitized **Decomposition of Ethylene***

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SOME years ago Le Roy and Steacie¹ proposed the following mechanism for the mercury shatter with the following mechanism for the mercury photosensitized decomposition of ethylene at room temperature:

$$Hg(^{1}S_{0}) + h\nu = Hg(^{3}P_{1})$$
(1a)

$$Hg(^{3}P_{1}) = Hg(^{1}S_{0}) + h\nu$$
 (1b)

$$Hg(^{3}P_{1}) + C_{2}H_{4} = C_{2}H_{4} + Hg(^{1}S_{0})$$
 (2)

$$C_2H_4^* + C_2H_4 = 2C_2H_4 \tag{3}$$

$$C_2H_4^* = C_2H_2 + H_2.$$
 (4)

The corresponding rate equation may be written in the form

$$1/(\phi q) = 1 + (k_2/k_3) (C_2H_4),$$
 (5a)

in which $\phi = (1/I_a)d(H_2)/dt =$ quantum yield of hydrogen production, and $q = \{k_b/k_1 + (C_2H_4)\}/(C_2H_4)$. From the quenching data of Steacie² the value of k_b/k_1 at 25°C is 0.367 mm.

This mechanism has recently been criticized by Darwent³ on the basis that the data may be fitted more accurately to the equation

$$\phi/(\gamma - \phi) = (k_3/k_2)/(C_2H_4) + (k_4/k_2)/(C_2H_4)^2,$$
 (5b)

in which γ is defined as the product of the "efficiencies" of reactions (1) and (4), and in which $k_4/(C_2H_4)$ is defined as the rate of heterogeneous decomposition of C2H4*. It should be noted, however, that at constant temperature each of the three parameters in Eq. (5b), γ , (k_3/k_2) , and (k_4/k_2) , was found to vary with the concentration of mercury in the cell, although only k_4 would be expected to change. A further difficulty was the fact that the maximum value of ϕ occurred at an ethylene pressure considerably higher than one would expect from quenching data.

We have re-investigated the reaction with emphasis on the accurate determination of rates and using a true resonance lamp as the light source, rather than a low pressure arc with noble gas carrier as used previously.^{1,3} The light originated as fluorescent radiation from a small quartz cell containing mercury vapor at a pressure of 1.8×10^{-4} mm and irradiated by a low pressure arc. The emission line should therefore be much narrower than that from a low pressure arc.

The radiation from the true resonance lamp was essentially all absorbed in a 60 mm cell containing mercury vapor at a pressure of 1.8×10^{-3} mm, whereas only 85 percent of the 2537A radiation from the low pressure arc was absorbed under the same conditions, although the arc was operated at less than half the current used previously.1 The absorption of light from the low-pressure arc increased to 95 percent, however, in the presence of 23.5 mm of ethylene, which suggests that pressure broadening of the absorption line is appreciable at these pressures.

If a low pressure arc were used one might expect, therefore, that the maximum would be shifted to higher ethylene pressures and that the rate vs (C_2H_4) curve would become distorted because of the effect of ethylene pressure on the rate of light absorption.



FIG 1. Effect of line structure on the rate curve, A^{\cdot} present data; B data of Le Roy and Steacie (reference 1) The ordinates are mm min⁻¹ ×10⁴ and mm hr⁻¹×10², respectively.

These effects would not be expected if the emission line were narrow relative to the absorption line. A comparison of our present results (curve A, Fig. 1) with those obtained previously¹ (curve B) appears to confirm this theory. With the true resonance lamp the maximum in the curve is quite sharp and occurs at the approximate position predicted from quenching data; in the previous work^{1,3} the maxima were very broad.

Darwent³ has suggested that some of the (³P₁) atoms are quenched to the metastable $({}^{3}P_{0})$ state by ethylene, and on this basis has predicted that the maximum rate should occur at ethylene pressures greater than two mm but at successively lower pressures as the mercury concentration is decreased. This interpretation is not borne out by the present measurements. We have found the maximum to occur at 2 mm with a mercury pressure of 1.8×10^{-3} mm, while he found it to occur at a considerably higher ethylene pressure with a mercury pressure of 1.8×10^{-4} mm.

We hesitate at this time to suggest a suitable modification of the original mechanism of Le Roy and Steacie, but it is interesting to note that whereas a plot of $1/(\phi q)$ vs (C₂H₄) using the data of Le Roy and Steacie or of Darwent is convex toward the (C_2H_4) axis even at the lowest pressures, the analogous plot using the present data is concave toward the (C_2H_4) axis. This might mean that deactivation, rather than decomposition of C₂H₄* can occur at the wall but further work will be necessary to settle the point.

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T Present address. Account research Canada ¹ D. J. Le Roy and E. W. R. Steacie, J. Chem Phys. 9, 829 (1941), ² E. W. R. Steacie, Can J. Research B18, 44 (1940). ³ B. de B. Darwent, J. Chem. Phys. 20, 1673 (1952).

Remarks on Mechanism of the $Hg({}^{3}P_{1})$ Photosensitized Decomposition of Ethylene

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HE communication from Mitchell and Le Roy indicates the necessity for correcting and explaining some points in my paper.

A. Pressure of ethylene for maximum rate (p_{max}) .—The statement, "The results given in Tables I and II seem to indicate that the maximum rate occurs at progressively decreasing pressures as the mercury concentration decreases" is misleading since there are no data which allow estimates to be made of p_{max} , in the experiments at the two highest mercury concentrations. The pertinent results at the lowest concentration of mercury were

pHg (mm Hg):	6.98	4.78	2.54
φH ₂ :	0.223	0.227	0.219

The accuracy of these results is probably not greater than ± 5 percent so that conclusions about p_{\max} would be very uncertain.

The statement quoted above was prompted by the fact that Le Roy and Steacie ($pHg=18\times10^{-4}$ mm) found $p_{max}=9$ mm, whereas in my experiments with $pHg = 1.8 \times 10^{-4}$ mm, p_{max} appeared to lie between 2.5 and 7.0 mm. I may add here that I was not primarily concerned, in that investigation, with the relationship between p_{max} and such factors as concentration of mercury.

B. Effect of (Hg) on p_{max} .—The statement was, "Since the rate of reaction (e) depends on the average distance through which the $({}^{3}P_{0})$ atoms diffuse before they strike a wall, it is not difficult to see, qualitatively, that the maximum rate of the reaction will occur at smaller pressures as the distance of diffusion is increased (i.e., as the concentration of mercury is decreased)." Reaction (e) represented the deactivation of $({}^{3}P_{0})$ atoms at the wall. The foregoing statement was offered as an explanation of (i) the effect of (Hg) on p_{max} , and (ii) the fact that p_{max} (in Le Roy and Steacie's experiments) was 9 to 10 mm. Now if $({}^{3}P_{0})$ atoms are formed and if they are capable, after many collisions, of causing

ethylene to decompose, they will have a greater chance of decomposing ethylene when they are formed far from the walls than when they are formed near to the wall. This means that, other conditions being equal, the quantum yield should increase with decreasing mercury concentration But it is difficult to see what effect, if any, the change in (Hg) should have on p_{max} , unless a detailed study is made of the kinetics. Furthermore, it is by no means certain that the $({}^{3}P_{0})$ atoms are capable of inducing the decomposition of ethylene and, if they are not, the change in mercury concentration should have no effect on either ϕ or p_{max} . Hence, I consider the statement in question to be inaccurate and it should be withdrawn.

Mitchell and Le Roy have found (1) that only 85 percent of the light from the low-pressure lamp is absorbed by a 60-mm path of mercury at 1.8×10^{-3} mm, and that this figure increases to 95 percent in the presence of 23.5 mm of ethylene; (2) that the maximum rate occurs at 2 mm with the resonance lamp, whereas Le Roy and Steacie had found it to occur at 9 mm with the broader line; (3) that with the resonance lamp the graph of $1/\phi H_2$ vs (C₂H₄) is concave towards the (C₂H₄) axis, whereas previous data with a broader line gave a convex curve. They conclude or suggest (1) that pressure broadening was important in the experiments with the broadened source; (2) that quenching to the metastable state $({}^{3}P_{0})$ is unimportant or at least not in accordance with the results; and (3) that excited ethylene molecules are deactivated and do not decompose on the wall.

Their first conclusion appears to be reasonable and may account for the change in p_{max} from the broad to the narrow line, though it is not obvious why this should be the case.

The second conclusion is not necessarily valid (it has been discussed above). The evidence for quenching to the metastable state was based on quite separate experiments¹ and, as mentioned previously, the photosensitized experiments may not be capable of providing evidence either for or against this type of quenching.

The third conclusion is perhaps the most interesting and important. If we accept Mitchell's and Le Roy's statement that 95 percent of the radiation is absorbed in a 60-mm path, when the pressure of ethylene is 23.5 mm, then in a 100-mm path such as was used in my experiments, we should expect that pressure broadening would be without effect provided that the ethylene pressure was above about 25 mm. Hence, if Le Roy and Steacie's mechanism were correct, there should be no difference above 25 mm between the results obtained with a broad or narrow line and the $1/\phi$ vs (C₂H₄) graph should be a straight line. There is no doubt that Le Roy and Steacie's results and my own, when plotted in this manner, deviated considerably from a straight line. It is true that my results, over a limited range (40 to 96 mm), appear to give a linear relationship between $1/\phi$ and (C_2H_4) ; however, the best line through those points extrapolate to $1/\phi \leq 0.5$ at $(C_2H_4)=0$. This is incompatible with the "original mechanism" which demands the extrapolated value of $1/\phi$ to be ≥ 1.0 and suggests strongly that the linear relationship over the limited range of pressure is only illusory and that we are really dealing with a continuous curve.

Mitchell and Le Roy now find that the $1/\phi vs$ (C₂H₄) curve, with the narrow line, deviates from linearity in the opposite sense to that obtained previously. Judging by their Fig. 1, the highest pressure was about 14 mm, and one wonders if they would continue to get this type of deviation at much higher pressure since the linear relationship is strictly valid only in the region of high pressures where the life time of $Hg({}^{3}P_{1})$ is quite negligible.

By using the narrow line, Mitchell and Le Roy have obtained the important result that $p_{max}=2$ mm, which is much more understandable than the previous value; but this can shed no light on the fate of the excited ethylene molecule unless the detailed kinetics are solved. Information about the fate of C₂H₄* can be obtained by working at high pressures where the kinetics become manageable and where pressure broadening should not complicate the picture.

¹ B deB Darwent and F. G Hurtubise, J. Chem. Phys. 20, 1684 (1952).