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Intramolecular Hydrogen Migration and Decomposition in the $\text{Hg}(^3\text{P}_1)$ Photosensitization of *trans*-Ethylene- d_2^{1a}

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The mercury photosensitized reaction of *trans*-ethylene- d_2 has been studied over a wide pressure range at 25° and 100°. Principal primary products are *cis*- $\text{C}_2\text{H}_2\text{D}_2$, *asym*- $\text{C}_2\text{H}_2\text{D}_2$, acetylene and hydrogen. Unimolecular rate constants for production of *asym*- $\text{C}_2\text{H}_2\text{D}_2$ and acetylene were measured. The former process is not appreciably altered by rise of temperature, but the latter is increased. At least two excited molecular states, first pointed out by Callear and Cvetanović, are involved in the over-all mechanism: the first is the lowest triplet state T of ethylene; the second is tentatively identified with a triplet ethylidene radical. Possible excited intermediates are discussed. The pressure dependence of acetylene formation is quantitatively accounted for on the basis of these excited states and the measured rate constants. A brief discussion of intermolecular secondary normal isotope effects in hydrogen split off from different isotopically substituted ethylenes is given.

The $\text{Hg}(^3\text{P}_1)$ photosensitized reactions of ethylene have attracted much interest since the work of LeRoy and Steacie^{2a}; important features include the role of the triplet state intermediate^{2a,b} and the nature of the pressure dependence of acetylene formation.^{2a,3,4} Callear and Cvetanović⁴ discovered that *trans*- and *asym*-ethylene- d_2 were formed on $\text{Hg}(^3\text{P}_1)$ photosensitization of *cis*-ethylene- d_2 , but did not study this intramolecular H transfer reaction in detail. More recently, Cvetanović and Doyle⁵ have obtained quantitative $\text{Hg}(^3\text{P}_1)$ photosensitization data on H migration in triplet butene-1 species with production of methylcyclopropane. They have pointed to a similarity between the two systems and have proposed that each of them must involve two electronically excited intermediate species.

In an effort to understand better the role of the excited states, we have measured the formation of acetylene, *cis*-ethylene- d_2 and *asym*-ethylene- d_2 upon $\text{Hg}(^3\text{P}_1)$ photosensitization of *trans*-ethylene- d_2 reactant, over a wide range of pressures at 25° and 100°. Secondary isotope effects for acetylene formation from the reactants, C_2H_4 , *trans*- $\text{C}_2\text{H}_2\text{D}_2$ and C_2D_4 , were reported earlier.⁶

Experimental

trans-Ethylene- d_2 was prepared in 99.3% isotopic purity, with ethylene- d_1 as the impurity.^{7a} C_2D_4 was prepared in 98% isotopic purity by catalytic deuteration of C_2D_2 . C_2H_4 was Phillips' research grade.

Runs were made at various initial pressures of an isotopic ethylene in 1 and 2 cm. diameter quartz vessels, with use of the lamp previously described.^{7b} The following technique was employed: The reactant was frozen into the vessel which contained a small droplet of Hg; the vessel was then warmed to 25° or 100°, thoroughly shaken and then irradiated for the desired period of time.

Secondary reactions resulting from formation of H atoms from H_2 product were kept low. Butane, a convenient measure of secondary processes, was usually barely measurable and at 25° was always less than 1% of the sample, except in one run in which it reached 2.4%.

Isotopic ethylene analyses were obtained with a Beckman IR-5 instrument by use of empirical calibration curves; acetylene and other products were measured by g.l.p.c. Isotopic acetylene composition was obtained from low-voltage parent-peak analysis on a Consolidated mass spectrometer calibrated with C_2H_2 and C_2D_2 .

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(2) (a) D. J. LeRoy and E. W. R. Steacie, *J. Chem. Phys.*, **9**, 829 (1941); E. W. R. Steacie, "Atomic and Free Radical Reactions," Reinhold Publishing Corp., New York, N. Y., 1954, p. 426. (b) K. J. Laidler, *J. Chem. Phys.*, **15**, 712 (1947).

(3) B. de B. Darwent, *ibid.*, **19**, 258 (1951).

(4) A. B. Callear and R. J. Cvetanović, *ibid.*, **24**, 873 (1956).

(5) R. J. Cvetanović and L. C. Doyle, *ibid.*, **37**, 543 (1962).

(6) B. S. Rabinovitch and D. W. Setser, *J. Am. Chem. Soc.*, **84**, 1765 (1962).

(7) (a) J. C. Douglas, B. S. Rabinovitch and F. S. Looney, *J. Chem. Phys.*, **23**, 315 (1955); (b) D. W. Setser, B. S. Rabinovitch and E. G. Spittler, *ibid.*, **35**, 1840 (1961).

These results for *trans*-ethylene- d_2 are independent of the efficiency of light absorption and quantum yield, since they may be expressed relatively in terms of the various fractions of the total products.

The secondary isotope effect data at 25° were obtained by performing successive runs in the same vessel for sets of the different isotopic ethylenes, at pressures in the region⁴ of total quenching. For a given group of runs, the stabilization and decomposition products were directly measured by first using *trans*-ethylene- d_2 as reactant; the following duplicate run with C_2H_4 and/or C_2D_4 as reactant was assumed to have the same total dosage of irradiation and quenching as the *trans*- $\text{C}_2\text{H}_2\text{D}_2$ sample, so that measurement of acetylene gave the decomposition amount, and stabilization could then be obtained by difference.

Results and Discussion

Intramolecular Hydrogen Migration and Hydrogen Split-off.—It is generally agreed that less than 1% of the quenching collisions between $\text{Hg}(^3\text{P}_1)$ and ethylene lead to direct formation of H atoms and vinyl radicals,^{2a,8}

TABLE I
SUMMARY OF CORRECTED PRODUCT AMOUNTS FROM REACTION OF $\text{C}_2\text{H}_2\text{D}_2$ AND $\text{Hg}(^3\text{P}_1)$

Pressure, cm.	Total %	25°		
		Relative product amounts—		
		<i>cis</i> ^a	<i>asym</i>	Acet.
0.5	24.0	8	3	82
1.0	33.5	12	8	68
2.0	21.9	16	15	53
4.0	13.7	22	18	36
4.0	30.3	24	17	36
5.0	19.5	26	21	27
6.0	22.0	30	20	20
8.0	14.2	31	21	16
8.0	27.1	33	21	14
16.0	37.8	41	13	6
16.0	52.6	41	12	6.1
50.0	38.6	46	5	2.3
76.0	31.2	48	3	0.6
100°				
0.5	19.3	7.5	6.8	78
0.5	50.3	6.8	4.5	82
1.0	40.0	8.8	7.1	74.6
2.0	20.7	12.9	8.9	65.4
2.5	29.6	16.1	14	53.6
5.0	16.4	23.2	16	37.5
7.6	14.4	24.6	20.4	30.4
10.0	15.8	27.3	20	25.3
15.0	35.6	37.5	14.6	10.8
30.0	29.7	43.6	8.5	4.5
40.0	18.4	42.4	10.1	5.2
50.0	29.7	45.5	6.4	2.7
76	69.2	47.6	3.5	1.1
152	58.4	49.5		1.06

^a An amount of *trans* equal to *cis* is also formed.

(8) (a) J. R. Majer, B. Mile and J. C. Robb, *Trans. Faraday Soc.*, **57**, 1343 (1960); (b) A. W. Tickner and D. J. LeRoy, *J. Chem. Phys.*, **19**, 1247 (1951).

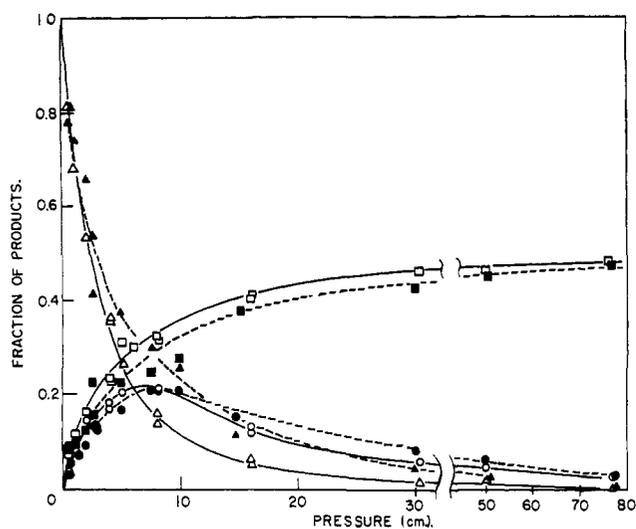


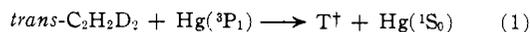
Fig. 1.—Fraction of products vs. pressure (cm.). At 25°, solid lines: *asym*-C₂H₂D₂, O; *cis*-C₂H₂D₂, □; acetylene, Δ. At 100°, dashed lines and filled symbols. For 25° and 100°, respectively, $R(\text{acet.}) = R(\text{asym})$ at 6.1 and 11.8 cm.; $R(\text{cis}) = R(\text{acet.})$ at 4.8 and 7.6 cm., $\omega_{\text{max}} = 6.5$ and 8.5 cm.

and that explanation of the products must be made in terms of excited intermediates.^{2a,4} The data are summarized in Table I.

The pressure dependence of the products acetylene, *asym*-C₂H₂D₂ and *cis*-C₂H₂D₂ formed in the photosensitized reactions of *trans*-C₂H₂D₂ at 25° and 100° are shown in Fig. 1. Product fractions are used since these are equivalent to relative quantum yields or relative steady-state rates. The stabilization products *cis*- and *asym*-ethylene-*d*₂ go to zero at zero pressure. Measurement of the (virtually sole) *cis*-product at sufficiently high pressures is a measure of the total number of excited *trans*-C₂H₂D₂ molecules formed. The figure shows that the reaction giving *asym*-C₂H₂D₂ is markedly pressure dependent and that the fraction of *asym* isomer goes through a maximum. This important fact coupled with other relations derived from the steady-state treatment is utilized below in order to evaluate the relative magnitudes of the rate constants for *asym*-C₂H₂D₂ and acetylene formation.

We also find in agreement with other workers that acetylene production follows something between an inverse linear^{2a} and quadratic³ function of pressure. The observed pressure dependence is shown in more detail in Fig. 2, and for the pressure range given there the data do follow the empirical relationship $(1/R)^{1/2} = A(1 + BP)$ previously proposed.⁴ LeRoy and Steacie had found a marked decrease in the quantum yield of hydrogen at low pressures; this was explained⁴ as being due to incomplete quenching of excited mercury and related phenomena. Our results which are independent of such effects confirm this explanation. One run was made in a 1-cm. diameter vessel packed with crushed quartz; no effect was apparent.

The salient features of the results, including the pressure dependence of acetylene formation, seem best described by the following scheme which is similar in some respects to one proposed by Callear and Cvetanović.⁴



where the dagger signifies electronic as well as vibrational excitation. Then

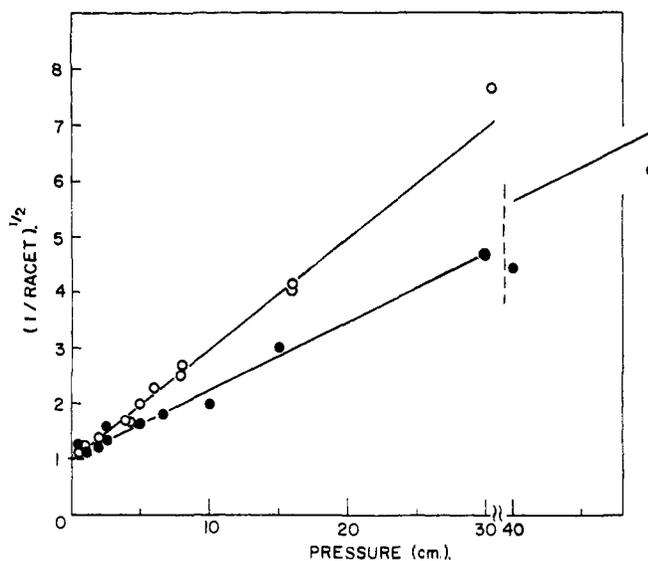
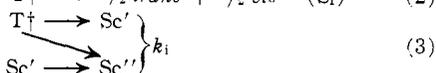
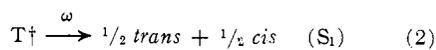
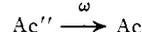
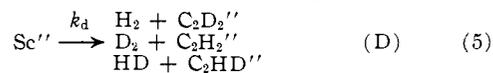
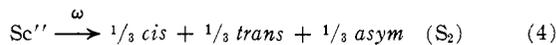


Fig. 2.— $1/R(\text{acet.})^{1/2}$ vs. pressure: O, 25°; ●, 100°.

where the primes symbolize possible electronic as well as vibrational excitation.



where eq. 4 and 5 may also be written for Sc' and where Ac'' etc. stands for the appropriate acetylene. Justification of the major points are now made. At least two excited ethylene states are necessary⁴ to explain the pressure dependence of acetylene formation; they are represented as $\text{T}\ddagger$ and Sc' , where reaction 3 represents some alternate possibilities. Their nature will be pursued later. The ratios of $\text{H}_2:\text{D}_2:\text{HD}$ are nearly the same with either *asym*-C₂H₂D₂ or *trans*-C₂H₂D₂ as reactant.⁹ This fact together with formation of *asym*-C₂H₂D₂ from *sym*-C₂H₂D₂ strongly implies that in both systems a common "scrambled" excited state, shown as Sc , is responsible for acetylene formation. Furthermore, if $\text{T}\ddagger$ decomposes to acetylene the rate of this process must be very small in order to preserve the proper pressure dependence for acetylene formation. This is discussed further when Fig. 4 is considered. A reverse step can be added to the mechanism. The



inclusion of 6 into the steady-state treatment which follows would complicate the resulting expressions but would not essentially alter their pressure dependence. Since the use of 6 makes it difficult to evaluate k_i and k_d , it will be omitted; however, its possible relevance may be remembered.

Steady-state treatment of $\text{T}\ddagger$ and Sc in reactions 1 through 5 yields the expressions a, b and c. It should be noted that collisional deactivation of $\text{T}\ddagger$ gives *cis*- and *trans*-C₂H₂D₂, while deactivation of Sc' gives *cis*-, *trans*- and *asym*-C₂H₂D₂.

$$R(\text{acet.}) = \frac{d(\text{acetylene})}{dt} = \frac{k_d k_i I}{(k_d + \omega)(k_i + \omega)} \quad (\text{a})$$

$$R(\text{asym}) = \frac{d(\text{asym-C}_2\text{H}_2\text{D}_2)}{dt} = \frac{1/3 \omega k_i I}{(k_d + \omega)(k_i + \omega)} \quad (\text{b})$$

$$R(\text{cis}) = \frac{d(\text{cis-C}_2\text{H}_2\text{D}_2)}{dt} = \frac{\omega I (3k_d + 2k_i + 3\omega)}{6(k_d + \omega)(k_i + \omega)} \quad (\text{c})$$

Figure 1 shows these respective rates (product fractions are identical to the relative rates) plotted against

(9) P. Ausloos and R. Gorden, Jr., *J. Chem. Phys.*, **36**, 5 (1962)

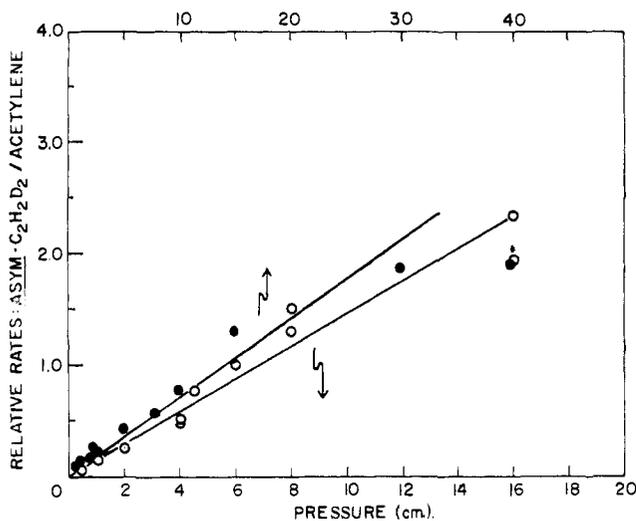


Fig. 3.—Relative rates of formation of products: *asym*/acetylene vs. pressure (cm.): O, 25°; ●, 100°.

pressure. The rate constants k_i and k_d are evaluated as follows.

Setting $R(\text{acet.}) = R(\text{asym})$ gives from eq. a and b, $k_d = \frac{1}{3} \omega_1$, where ω_1 is the collision frequency at the pressure (6.1 cm. at 25°, and 11.8 cm. at 100°; Fig. 1) where these rates are equal. Values are $k_d = 3.27 \times 10^8$ and $6.31 \times 10^8 \text{ sec.}^{-1}$, respectively, using a collision diameter of 4.95×10^{-8} cm. for both ethylene and the excited states (the latter may very well be larger). An alternative way of finding k_d is from the function $R(\text{asym})/R(\text{acet.}) = \omega/3k_d$. The data are plotted in Fig. 3 and they follow this expression within experimental error. The slopes give $k_d = 3.7 \times 10^8$ and $6.05 \times 10^8 \text{ sec.}^{-1}$. Average values of $k_d = 3.5 \times 10^8 \text{ sec.}^{-1}$ at 25° and $6.2 \times 10^8 \text{ sec.}^{-1}$ at 100° are used.

The rate constant k_i was obtained by solving the equation $dR(\text{asym})/d\omega = 0$, which gives $\omega^2 = k_i k_d$. Values for ω_{max} of 6.5 cm. and 8.5 cm. obtained from Fig. 1, combined with the previous evaluation of k_d , give $k_i = 3.1 \times 10^9$ and $3.04 \times 10^9 \text{ sec.}^{-1}$ at 25° and 100°, respectively.

The relative values for k_i and k_d can be applied to eq. d, which results from setting $R(\text{cis}) = R(\text{acet.})$.

$$3k_d + 2k_i + 3\omega = 6k_d k_i / \omega \quad (\text{d})$$

The above values of k_i and k_d satisfy d to within $\sim 10\%$.

The mechanism also gives eq. e. A plot of S_1/S_2

$$S_1/S_2 = k_d/k_i + \omega/k_i \quad (\text{e})$$

vs. ω is not sufficiently sensitive to give the correct magnitude for the intercept, *i.e.*, of k_d , although the slopes give values of k_i at 25° and 100° of $\sim 3.5 \times 10^9$ and $2.9 \times 10^9 \text{ sec.}^{-1}$, in reasonable agreement with the above values. A plot of $R(\text{cis})/R(\text{asym})$ vs. ω should follow eq. f. Such a graph emphasizes experimental errors and possible over-simplification of the mechanism;

$$R(\text{cis})/R(\text{asym}) = 1 + \frac{3}{2} k_d/k_i + \frac{3}{2} \omega/k_i \quad (\text{f})$$

perhaps other processes, such as reaction 6, should be included. Our data are not sufficiently extensive or accurate to test these more detailed aspects.

Consider next the pressure dependence of acetylene formation in the present formulation. Callar and Cvetanović pointed out that existing data follow a $1/R(\text{acet.})^{1/2}$ vs. ω relation over most of the pressure range. Our results in Fig. 2 also fit this relation. Equation a shows that a linear relation in Fig. 2 is only rigorously true if $k_i = k_d$; but, for limited pressure ranges, certain disparities of values for k_i and k_d are permitted such that the linear relation will still roughly hold.⁴ For our individual rate constants, which are in

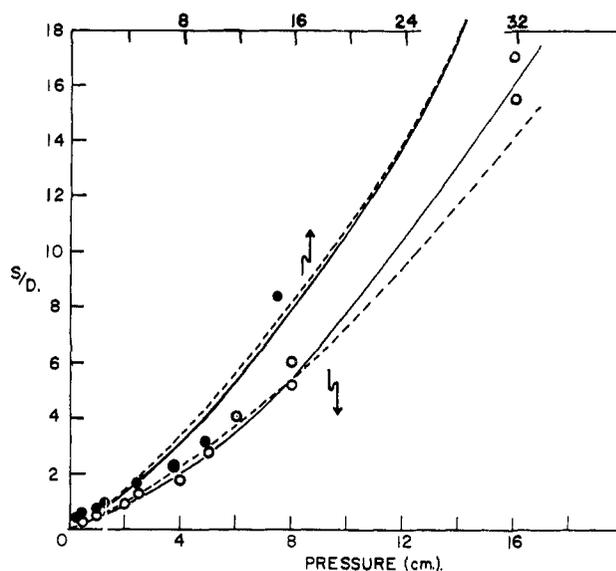


Fig. 4.—Total stabilization/decomposition vs. pressure: 0.25°; ●, 100°; calculated curves.

the ratio of 10:1 at 25°, a 10% deviation from linearity in Fig. 2 should occur at a pressure of 30 cm.; furthermore the points should lie below the extrapolated low pressure line. The high pressure data at 100° decreases in the expected direction.

A more sensitive test of the acetylene pressure dependence is a plot of S/D vs. pressure (Fig. 4) according to eq. g.

$$(S_1 + S_2)/D = S/D = \frac{\omega(k_i + k_d)}{k_i k_d} + \frac{\omega^2}{k_i k_d} \quad (\text{g})$$

The dotted line in Fig. 4 is the predicted line obtained from the above values for k_i and k_d . The predicted variation with pressure is in general agreement with experiment; a significant deviation at still higher pressure reflects the inadequacy of the present mechanism and suggests that a subsidiary mechanism for acetylene formation exists which could possibly involve vinyl radicals.⁸

Nature of Excited States.— T^+ undoubtedly represents the lowest triplet state.² Collisions with ethylene appear to efficiently degrade the electronic excitation as well as vibrational excitation.¹⁰ The principal question concerning the interpretation of the data is the identity of the Sc species—whether ethylene or ethylidene species (formation and hydrogen split-off from the latter automatically producing scrambling), whether in a singlet or triplet electronic state, and whether Sc' and Sc'' actually both enter the mechanism. Some relevant observations from the literature may first be considered. Frey¹¹ proposes that a singlet state ethylidene radical¹² does not decompose directly to acetylene but is rapidly converted to vibrationally excited ethylene which then undergoes split-off. Indeed the decomposition of (presumably singlet) ethylidene radicals, produced by photolysis of diazoethane at 2500–2700 Å. by Brinton and Volman,¹³ gives a ratio of $C_2H_4:C_2H_2$ at 20 cm. pressure which is very close to that found here; *i.e.*, k_d is nearly the same in both studies. By analogy with the known thermochemistry¹⁴ of the methylene radical-diazomethane photolysis system, and from reasonable estimates of $\Delta H_f(\text{CH}_3\text{CH})$, a

(10) D. W. Setser, D. W. Placzek, R. J. Cvetanović and B. S. Rabinovitch, *Can. J. Chem.*, **40**, 2179 (1962).

(11) H. M. Frey, *J. Chem. Soc.*, 2293 (1962).

(12) G. B. Kistiakowsky and B. H. Mahan, *J. Am. Chem. Soc.*, **79**, 2414 (1957).

(13) R. K. Brinton and D. H. Volman, *J. Chem. Phys.*, **19**, 1394 (1951).

(14) D. W. Setser and B. S. Rabinovitch, *Can. J. Chem.*, **40**, 1425 (1962).

singlet ethylene molecule formed from ethylidene in Brinton and Volman's system should have an energy > 100 kcal. mole, as in the present system.

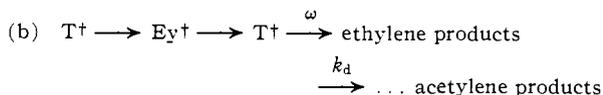
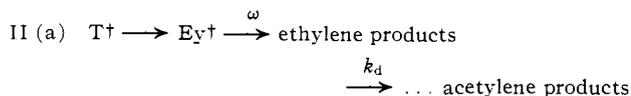
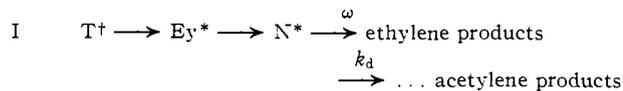
Since methylcyclopropane is formed on addition of singlet ethylidene radical to the ethylene double bond,¹¹ an extensive (negative) search was made for it over a wide pressure range. This eliminates the possibility of the Sc" species being the singlet ethylidene since radical reaction 4 would otherwise give rise to the methyl cyclopropane.

If, instead, Sc" were the vibrationally excited singlet ethylene molecule, then to explain the isotopically scrambled ethylene and acetylene products it must either be preceded by ethylidene formation or be a highly vibrationally excited ground N state which undergoes internal scrambling—in contradistinction to the lack of observed scrambling at ≈ 65 kcal. of vibrational excitation for the N state,^{7a} or for the presently observed T† state. Although by no means identical systems, very high energy photolysis work with ethylenes¹⁵ does not show efficient scrambling and is suggestive that the latter of the above-mentioned alternatives is unlikely.

The reaction process 3 described by the rate constant k_i is virtually unaffected by the rise of temperature from 25° to 100°, while reactions 5, described by the composite constant k_d , are notably enhanced by the small increase (~ 0.5 kcal. mole⁻¹) in internal energy of the reactant ethylene with rise of temperature. This could suggest that reaction 3 is not a conventional unimolecular rearrangement process but involves a barrier-less transition between potential energy surfaces.

It appears that Sc" is attacked by oxygen.¹⁰ This could indicate that Sc" is a triplet ethylidene state,¹⁶ although the possibility of an appreciable reactivity of O₂ with a singlet state ethylene species, vibrationally excited to >100 kcal. mole⁻¹, has not been disproved either.

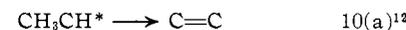
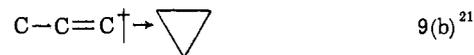
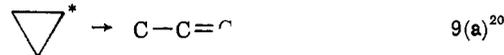
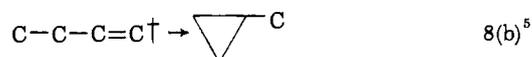
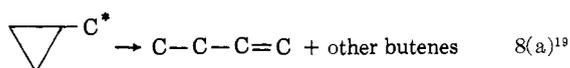
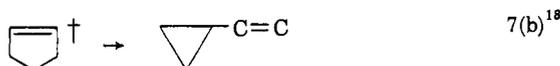
The present work cannot decide these issues. The most probable schemes are I and II where the distinction between a and b are unimportant but could help explain lack of addition of Ey† to the double bond, although this may well be inefficient.¹¹ A dagger signifies triplet state, Ey represents ethylidene, N and T have their usual meaning and an asterisk signifies a highly vibrationally excited singlet state. II (b) is in addition to II (a) and not in place of it.



In addition to the previous discussion, there is a general pattern of rearrangement behavior of triplet state olefin systems, which reverses the reactions of vibrationally excited singlet cyclopropane and may support scheme II. Some relevant examples are listed

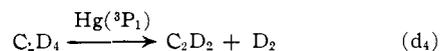
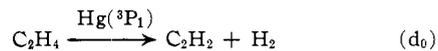
(15) A. Okabe and J. R. McNesby, *J. Chem. Phys.*, **36**, 601 (1962).

(16) J. P. Chesick, *J. Am. Chem. Soc.*, **84**, 448 (1962), has shown that J. R. Majer, B. Mile and J. C. Robb, *Trans. Faraday Soc.*, **57**, 1692 (1961), were wrong in the contention that the species formed from Hg(³P₁) + ethylene added across the C-H bond in propane to give pentanes. Triplet methylene does not appear to add to the C-H bond [H. M. Frey, *J. Am. Chem. Soc.*, **82**, 5947 (1960)].

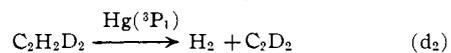


In the last case, ethylidene formation is the analogous to ring formation for the other members of the series. In every case, the presumed triplet state system was produced by mercury photosensitization. Callear and Cvetanović⁴ tentatively suggested Ey† as the scrambling intermediate.

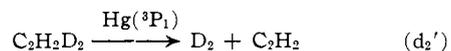
Secondary Isotope Effects in H₂ Split-off from Ethylene.—In a preliminary communication we noted that the Hg(³P₁) photosensitized decomposition of various deuterioethylenes provides information on the secondary deuterium kinetic isotope effect for acetylene formation. The reported⁴ high pressure data on C₂H₄ and C₂D₄ were interpreted as yielding a ratio for the secondary isotope effects in the over-all reactions d₀ and d₄,



after correction for the primary kinetic isotope effect for H₂ and D₂ split-off, of $k_{d_0}/k_{d_4} \approx 2$. An additional source of information, which formally avoided the primary isotope effect correction, was the comparison of the relative rates for the reaction pairs d₀ and d₂



and d₂' with d₄



after correction for reaction path degeneracy and concurrent modes of rupture of C₂H₂D₂ by H₂, HD and D₂ split-off.

We now find with the data at hand a slightly altered value for the average of k_{d_0}/k_{d_2} and k_{d_2}/k_{d_4} of 1.3, rather than our earlier value 1.39. For k_{d_0}/k_{d_4} we have 1.6 rather than 1.9 reported previously. The average of our value for d₀/d₄ with that of ref. 4 is 1.8 which is still of substantial magnitude.

The values for k_{d_0}/k_{d_2} and k_{d_2}'/k_{d_4} were reported as a single average originally, since analytical inaccuracy

(17) (a) H. M. Frey, *Trans. Faraday Soc.*, **58**, 516 (1962); (b) M. C. Flowers and H. M. Frey, *J. Chem. Soc.*, 3547 (1961).

(18) W. A. Gibbons, W. F. Allen and H. E. Gunning, *Can. J. Chem.*, **40**, 568 (1962).

(19) (a) J. N. Butler and G. B. Kistiakowsky, *J. Am. Chem. Soc.*, **82**, 759 (1960); (b) J. P. Chesick, *ibid.*, **82**, 3277 (1960).

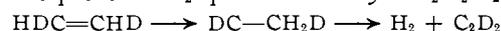
(20) T. S. Chambers and G. B. Kistiakowsky, *ibid.*, **56**, 399 (1934); G. B. Kistiakowsky and K. Sauer, *ibid.*, **78**, 5699 (1956).

(21) D. W. Placzek, unpublished data, found a small amount of cyclopropane ($\sim 0.5\%$ of total products) in this reaction. P. Kebarle and M. Avrahami (private communication), find such as "a very minor product at most."

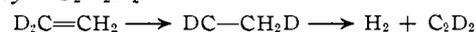
(see below, also) in the measurements for $C_2H_2D_2$, which enter into both d_0/d_2 and d_2'/d_4 , thereby tend to cancel. However, the latter ratio is larger than the first by an amount which seems greater than the rather considerable experimental error.

Further detailed discussion is not of value, since apart from the analytical inaccuracy, interpretation of the data for this acetylene formation reaction in terms of isotope effects is further restricted in the following way. Some of the data previously discussed⁶ referred of necessity to high pressures: In the absence of relative or absolute quantum yields ϕ , relative rates of decomposition (D) by H_2 split-off for the various ethylenes could be inferred only at high pressures where the stabilization (S) of the excited species became effectively constant as $\phi \rightarrow 0$. An apparent rate constant k_a for ethylene decomposition by H_2 or D_2 split-off was defined as $k_a = \omega D/S$, where ω is the collision number. For constant ω , then $k_{aH_2}/k_{aD_2} = D_{H_2}/D_{D_2}$ at high pressures, if the assertion of linearity between k_a and D were to hold. However, we noted that since the reported⁴ rate expression, *i.e.*, $1/R^{1/2} = A(1 + BP)$, fits the data on acetylene production rather well, that a *simple* linear relation between the relative apparent rate constant k_a for formation of acetylene and the elementary rate constant k_d of eq. 5 did not apply (*i.e.*, $k_a \neq \omega \cdot D/S$). The justification for using this phenomenon was that the rate k_a *did* involve k_d in an important way and is worthy of consideration. This is indeed so, but in view of eq. 5 above it is clear that

these observed ratios are not measurements of pure isotope effects well suited for theoretical interpretation (nor indeed are the primary isotope effects). In addition, it has been noted by Ausloos and Gorden⁹ that not all the isotope effects involved are understood. For example, they found a ratio of $C_2H_2:C_2HD:C_2D_2$ formation from *asym*- $C_2H_2D_2$ of 1.09:4.65:2.0 different from that from *sym*- $C_2H_2D_2$ (0.99:5.85:2). Our average rate ratio for *trans* split-off of $H_2:HD:D_2$ is 2.0:4.8:1.11 over the range 1–16 cm.; for *cis*-ethylene- d_2 Callar and Cvetanović have an average of 2.0:5.94:1.01 from H_2 analysis (and 2.0:4.75:0.98 from isotopic acetylene analyses which are presumably less reliable). Ausloos and Gorden suggested that other mechanisms of decomposition of mercury-photosensitized ethylene should be considered beside that of ref. 4. It may be noted, however, that whereas H migration to form ethylidene precedes H_2 split-off from *sym*- $C_2H_2D_2$



that, by contrast, D migration precedes H_2 split-off from *asym*- $C_2H_2D_2$



Thus a small isotope effect for the migration step could possibly reconcile the data of Ausloos and Gorden for *asym*.

More recently, Cvetanović, Falconer and Rabino-vitch cited secondary intermolecular isotope effects on $Hg(^3P_1)$ photosensitization of butene-1 and butene-1- d_8 of magnitude 2.6–2.9.⁵

[CONTRIBUTION FROM FRICK CHEMICAL LABORATORY, PRINCETON UNIVERSITY, PRINCETON, N. J.]

Nitriles and Isonitriles as Proton Acceptors in Hydrogen Bonding: Correlation of $\Delta\nu_{OH}$ with Acceptor Structure¹

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Infrared spectral shifts due to hydrogen bonding between proton donors and nitriles with widely differing substituents correlated very well with Taft's σ^* -constants. The range of σ^* -constants for the compounds studied extended from +2.65 (for CCl_3CN) to -0.48 (for cyclopropyl cyanide). The spectral shifts for these extremes were, respectively, 62 to 173 cm^{-1} with phenol as proton donor. Isonitriles have also been examined as hydrogen bonding bases. Molecular structure evidence indicates the preferred form of these compounds

to be $R-\overset{+}{N} \equiv \overset{-}{C}$; the strong hydrogen bond observed to this group is most probably to carbon and not to nitrogen. A Taft correlation was also obtained with isonitriles. The compounds studied ranged from *tert*-butylisonitrile ($\sigma^* = -0.30$) to phenylisonitrile ($\sigma^* = +0.60$). The spectral shifts, from 245 to 203 cm^{-1} , respectively, with phenol as proton donor, were larger than those with nitriles. The Hammett equation correlated the spectral shifts of aromatic nitriles and aromatic isonitriles over a limited range of compounds studied. Because of geometrical limitations, intramolecular hydrogen bonding (found only in α - and β -hydroxynitriles) was weak and involved the π -electrons of the $C \equiv N$ triple bond and not the nitrogen atom.

Intermolecular hydrogen bonding between hydroxylic proton donors $Y-OH$ and proton acceptors $B-R$ has been studied extensively by infrared spectroscopic methods.⁴ The spectral shift, $\Delta\nu_{OH}$, is defined as the difference in OH stretching frequency of free $Y-OH$ and hydrogen bonded $Y-OH \cdots B-R$. The magnitude of $\Delta\nu_{OH}$ will be influenced by variations in B , the proton acceptor group, in Y ⁵ and in R .⁶ There has been no systematic study of the effect of variations of R on

$\Delta\nu_{OH}$. Caldow and Thompson investigated the systems $R-X \cdots HCN$ (and DCN) where $X = Cl, Br, I$ and NO_2 ; $C_6H_5C \equiv CH \cdots O=C(CH_3)R$; and $C_6H_5-C \equiv CH \cdots N \equiv CR$.⁷ An approximately linear relationship was found between ν_{CH} , the position of the bonded C-H (or C-D) peak, and the Taft inductive factors, σ^* ,⁸ for the groups R . However this study suffers from some deficiencies. Weak proton donors were used resulting in small ranges of frequency shifts—only about 40 cm^{-1} —with changes in R . The measurements were carried out in pure liquid proton acceptors, *i.e.*, not in a constant environment.⁹ In some cases the CH bands studied overlapped partially with bands

(1) Paper IX of a series on hydrogen bonding; paper VIII, *J. Am. Chem. Soc.*, **85**, in press (1963). This work was taken from the Ph.D. Thesis of Adam Allerhand, Princeton University, 1962; preliminary communication, *J. Am. Chem. Soc.*, **84**, 1322 (1962).

(2) Merck Foundation Fellow, 1960–1961; Esso Foundation Fellow, 1961–1962.

(3) Alfred P. Sloan Research Fellow.

(4) G. C. Pimentel and A. L. McClellan, "The Hydrogen Bond." W. H. Freeman and Co., San Francisco, Calif., 1960.

(5) An extensive study of the effect of variation in Y upon $\Delta\nu_{OH}$ has been carried out; J. Greer, unpublished.

(6) W. Gordy and S. C. Stanford, *J. Chem. Phys.*, **8**, 170 (1940); **9**, 204 (1941).

(7) G. L. Caldow and H. W. Thompson, *Proc. Roy. Soc. (London)*, **A254**, 1 (1960).

(8) R. W. Taft, Jr., in M. S. Newman, Ed., "Steric Effects in Organic Chemistry," J. Wiley and Sons, Inc., New York, N. Y., 1956, Chapter 13.

(9) Spectral shifts have frequently been measured by the undesirable technique of using the proton acceptor as solvent; instead, such studies should be carried out in an inert solvent with as low a concentration of proton acceptor as possible.^{10,11}