PROBLEMS IN THE DETERMINATION OF RATE CONSTANTS FROM PHOTOCHEMICAL EXPERIMENTS[1]

JACK G. CALVERT

Department of Chemistry, The Ohio State University, Columbus 10, Ohio

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I. INTRODUCTION

A major interest in the determination of reliable estimates of the rate constants of free-radical reactions arises in the relationship of these quantities to the bond-dissociation energies in molecules and the thermodynamic properties of the free radicals themselves. Although it is not generally recognized, the presently "accepted" values for the bond-dissociation energies in the aldehyde, ketone, and many of the hydrocarbon molecules are based on a limited body of somewhat conflicting, rather tenuous data. Most obvious of the conflicts is that between bond-energy data based on photochemical kinetic estimates and that derived from electron impact, thermal kinetic estimates, etc. Typical of the reactions about which there is much confusion are the following, which will be considered in this discussion:

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$$sec\text{-}C_4H_9\cdot \rightarrow CH_3\cdot + C_3H_6 \qquad (1)$$

$$n\text{-}C_3H_7\cdot \rightarrow CH_3\cdot + C_2H_4 \qquad (2)$$

$$H\dot{C}O + M \rightarrow H\cdot + CO + M \qquad (3)$$

$$CH_3\dot{C}O\ (+ M) \rightarrow CH_3\cdot + CO\ (+ M) \qquad (4)$$

The current best estimates of the enthalpy change for these reactions as derived from photochemical kinetic studies of the forward and reverse reactions are: $\Delta H_1 = 17$; $\Delta H_2 = 11$; $\Delta H_3 = 14$; $\Delta H_4 = 10$ kcal./mole. Contrast these with the enthalpy values based on "reasonable" thermal data, electron-impact experiments, etc.: $\Delta H_1 = 24$; $\Delta H_2 = 26$; $\Delta H_3 = 27$; $\Delta H_4 = 18$ kcal./mole. The origin of these differences has not been clear, but since the photochemical kinetic estimates are the most involved and indirect determinations, they are commonly considered to be least reliable. However, there are sufficient problems and uncertainties associated with all of the methods to make an unambiguous choice between the divergent data very difficult. Certainly a reëvaluation of the accuracy and possible errors in the photochemical determinations upon which the lower enthalpy data are based is imperative.

The many advantages of the photochemical techniques of the generation of radicals often tend to obscure the several inherent difficulties associated with them. The possible complication of "hot," or nonthermally equilibrated, radicals has been recognized for years as a major source of inaccuracy in a number of systems. The complication is most common in the systems containing molecules which have relatively weak chemical bonds and absorb quanta of light whose energy is much in excess of this bond energy. These molecules decompose into radicals or atoms which carry off the excess energy as translational, rotational, vibrational, or electronic excitation. The reactions which occur in the photolysis of the metal alkyls (e.g., diethylmercury), the alkyl iodides (e.g., methyl iodide), etc., show evidence of "hot" radicals. This problem is usually readily recognized and can often be controlled in gas-phase experiments through the use of a large excess of moderating gas.

However, there are several more subtle difficulties in the determination of rate constants which plague the photochemical investigator. Among these is one which will be discussed in some detail. Presumably it results during the process of internal conversion and degradation of electronic energy contained in a molecule. A consideration of the detailed mechanism of this process is helpful in resolving some of the disagreements between photochemical data and thermal data for reactions 1 and 2. New kinetic data for reaction 2, which were derived in systems free from this and many other of the complications of most photochemical systems, will be reviewed.

II. The Decomposition Reaction of the *sec*-Butyl Free Radical

$$sec\text{-}C_4H_9\cdot \rightarrow CH_3\cdot + C_3H_6 \qquad (1)$$

There are two independent photochemical kinetic estimates which support the value $E_1 \cong 23$ kcal./mole (6, 12). At the time that this work was done, the authors believed the activation energy for the reverse reaction to be very low (about 2 kcal./mole), so that the value $E_1 \cong 23$ was considered consistent with the thermal estimates of $\Delta H_1 \cong 24$ kcal./mole. However, there has accumulated in recent years a considerable body of evidence which proves much higher values of activation energies for the addition of radicals to double bonds than was generally accepted previously. Thus Mandelcorn and Steacie (14) estimate that $E_{-1} \cong 6$ kcal./mole. The value $\Delta H_1 \cong E_1 - E_{-1} \cong 17$, which kinetic data suggest, can no longer be considered as equal within the experimental error to the thermal estimates of near 24 kcal./mole. Obviously a critical reëvaluation of the photochemical kinetic estimates is in order.

A. ESTIMATES OF THE RATE OF DECOMPOSITION OF THE *sec*-BUTYL RADICAL FROM THE MERCURY-PHOTOSENSITIZED DECOMPOSITION OF *n*-BUTANE

The first of the estimates was derived from the mercury-photosensitized decomposition of *n*-butane (6). Both *n*-butyl and *sec*-butyl radicals were generated simultaneously in these experiments. However, it seems probable that the methane and propylene found in the decomposition products arise solely from the *sec*-butyl radical, while the ethane and ethylene come only from the decomposition of the *n*-butyl radical. The fact that migration of a hydrogen atom, which is improbable in a homogeneous gas-phase system, must accompany the reactions, $n\text{-}C_4H_9\cdot \rightarrow CH_3\cdot + C_3H_6$ and $sec\text{-}C_4H_9\cdot \rightarrow C_2H_5\cdot + C_2H_4$, and evidence from the product distribution in the pyrolysis of di(*sec*-butyl)mercury and di(*n*-butyl)-mercury lead one to this view (11). Hence the data of Bywater and Steacie on methane should give information specifically about reaction 1. From the temperature dependence of methane formation in experiments at constant absorbed light intensity and pressure, they derive the activation energy, 23 kcal./mole. If the only fate of methyl radicals is that of abstraction of hydrogen from butane, then it follows that

$$\frac{d[CH_4]}{dt} = [sec\text{-}C_4H_9\cdot]\, k_1$$

Bywater and Steacie interpret the rate data for methane at different temperatures as a measure of k_1 in these experiments; this is equivalent to assuming that the steady-state concentration of the *sec*-butyl radical is equal over the temperature range of these experiments (250–375°C.). It would be interesting to test this hypothesis by monitoring the rates of formation of 3,4-dimethylhexane formed in this system. It seems more likely to this author that some decrease in the steady-state concentration of the *sec*-butyl radical will occur as the temperature is raised and the stability of the radical is lowered. A concentration decrease of only a factor of 2 over the temperature range involved would cause the calculated activation energy to be low by 5 kcal. The unambiguous quantitative interpretation of these results is difficult at present, but from the evidence at hand no great confidence can be placed in the assignment of the measured activation energy to reaction 1.

B. ESTIMATES OF THE RATE OF DECOMPOSITION OF THE *sec*-BUTYL RADICAL FROM THE PHOTOLYSIS OF 2-METHYLBUTANAL

In the second study of reaction 1, Gruver and Calvert (12) photolyzed 2-methylbutanal at 3130 A. The formation of butyl radicals and their reaction under these conditions were in accord with the following mechanism:

$$sec\text{-}\mathrm{C_4H_9CHO} + h\nu \rightarrow sec\text{-}\mathrm{C_4H_9}\cdot + \mathrm{H\dot{C}O} \tag{I}$$

$$sec\text{-}\mathrm{C_4H_9}\cdot + \mathrm{C_4H_9CHO} \rightarrow n\text{-}\mathrm{C_4H_{10}} + \mathrm{C_4H_9\dot{C}O} \tag{5}$$

$$sec\text{-}\mathrm{C_4H_9}\cdot \rightarrow \mathrm{CH_3}\cdot + \mathrm{C_3H_6} \tag{1}$$

$$2sec\text{-}\mathrm{C_4H_9}\cdot \rightarrow \mathrm{C_8H_{18}} \tag{6}$$

$$\mathrm{CH_3}\cdot + \mathrm{C_4H_9CHO} \rightarrow \mathrm{CH_4} + \mathrm{C_4H_9\dot{C}O} \tag{7}$$

$$\mathrm{C_4H_9\dot{C}O} \rightarrow sec\text{-}\mathrm{C_4H_9}\cdot + \mathrm{CO} \tag{8}$$

At temperatures above 250°C. the major source of methane is reaction 1 followed by reaction 7. At lower temperatures a small amount of methane was formed and attributed to a minor primary reaction:

$$sec\text{-}\mathrm{C_4H_9CHO} + h\nu \rightarrow \mathrm{CH_3}\cdot + \cdot\mathrm{C_3H_6CHO} \tag{IIa}$$

or

$$sec\text{-}\mathrm{C_4H_9CHO} + h\nu \rightarrow \mathrm{CH_4} + \mathrm{C_3H_5CHO} \tag{IIb}$$

From this choice of mechanisms the rate function 9 was derived.

$$\frac{(\Phi_{\mathrm{CH_4}} - \phi_{\mathrm{II}})I_a^{1/2}}{(\Phi_{\mathrm{C_8H_{18}}})^{1/2}} = \frac{k_1}{k_6^{1/2}} \tag{9}$$

ϕ_{II} was estimated from the low-temperature values of $\Phi_{\mathrm{CH_4}}$. The temperature dependence of 9 gave $E_1 - E_6/2 \cong 23$ kcal./mole.

Recently a study of the iodine-inhibited photolysis of 2-methylbutanal was made (13). *sec*-Butyl iodide was a major product, but neither methyl iodide nor methane could be found. Obviously the hypothesis of the formation of methyl radicals or methane in a primary process is untenable. One also cannot explain the results in terms of the formation of "*hot*" *sec*-butyl radicals in the primary process I with subsequent decomposition, since propylene is not a product of the uninhibited photolysis at the lower temperatures.

1. Proposed revised mechanism of methane formation in the photolysis of 2-methylbutanal

It appears reasonable to suggest that methyl radicals from the photolysis of 2-methylbutanal arise from the decomposition of a vibrationally excited 2-methylbutanal molecule formed by the internal conversion of electronic excitation; the lifetime of the vibrationally excited molecule may be sufficient so that rather complete deactivation of the excitation is effected in the experiments with added iodine. The relatively small energy separation of the vibrational modes of molecu-

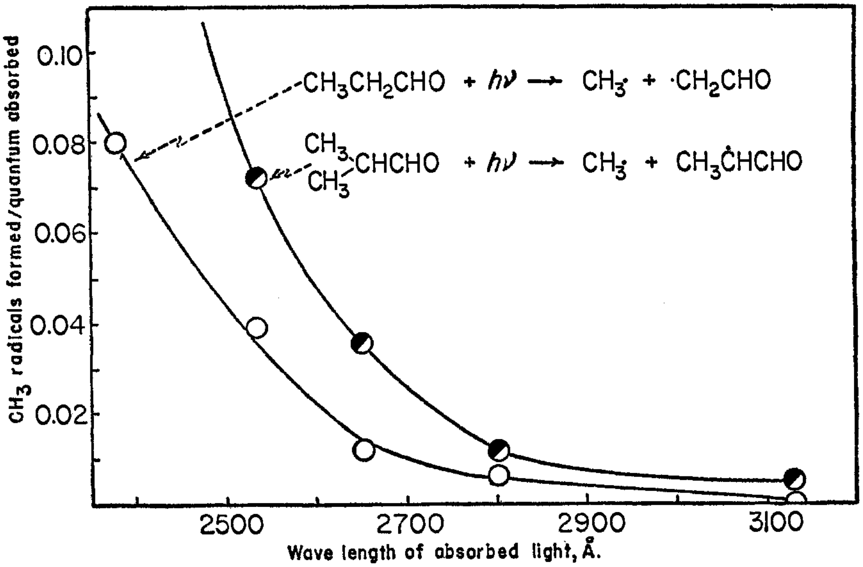

FIG. 1. The quantum efficiency of the formation of methyl radicals in the uninhibited photolyses of propionaldehyde (3) and isobutyraldehyde (1) at 25°C. as a function of the wavelength of the absorbed light.

lar iodine is presumed to make it an effective agent to remove vibrational excitation (16). In experiments up to 127°C. the iodine-inhibited photolyses of 2-methylbutanal show that about 20 per cent of the electronically excited molecules formed do not lead to observed products. Presumably these are involved in internal conversion processes and are collisionally deactivated.

2. *The mechanism of "down-chain" splits in the photolysis of other aldehydes*

It seems likely to the author that many other of the molecular fragmentations which occur well down the chain from the absorbing group are not primary processes, as has often been proposed, but may have their origin in a decomposition of vibrationally excited molecules such as he suggested for the 2-methylbutanal system. In uninhibited photolyses both propionaldehyde (3) and isobutyraldehyde (1) form small quantities of methane at 3130 A. even at the lower temperatures, but methyl iodide and methane have not been detected in the products of the iodine-inhibited experiments at this wavelength. The variation in the quantum efficiency of methane formation with wavelength at 25°C. is shown for these aldehydes in figure 1. It is interesting that at each wavelength about twice as many methyl radicals are formed from isobutyraldehyde as from propionaldehyde. This may be related simply to the probability of the accumulation of the necessary vibrational quanta in a C—CH_3 bond, which then ruptures and leads to the formation of methyl radicals. In isobutyraldehyde there are two such bonds, while propionaldehyde has but one. This picture is interesting, but it is probably an oversimplification, since the fraction of these molecules which are deactivated by collision or internal conversion processes at 3130 A. is estimated from iodine-inhibition experiments to be 0.49 for propionaldehyde and only 0.24 for isobutyraldehyde. In line with the correlation of the number of α-methyl groups with the quantum efficiency of a methyl-forming reaction are the preliminary results on the photolysis of pivalaldehyde, $(CH_3)_3CCHO$ (2). It has been shown qualitatively that this compound gives a higher efficiency of formation of methyl radicals in the uninhibited photolyses at a given wavelength and temperature than either propionaldehyde or isobutyraldehyde.

It is likely that the α-methyl group is the one lost in the photolysis of 2-methylbutanal also, since Φ_{CH_4} from the photolysis of butyraldehyde at 3130 A. is negligible up to 150°C. There is no ethane in the products of the photolysis of 2-methylbutanal or butyraldehyde, so the analogous split of α-ethyl groups does not appear to occur.

3. Revision of the estimate of the rate of decomposition of sec-butyl radicals in the light of the revised mechanism of methane formation at low temperatures

The present interpretation of methane formation in the photolysis of 2-methylbutanal requires a revision of the calculation method used by Gruver and Calvert to derive k_1. If the low-temperature methane has its origin in the decomposition of a vibrationally excited aldehyde molecule, then the assumption of constancy of the efficiency of this process with increase in temperature must be questioned. The data show that the process is temperature dependent: $\Phi_{CH_4} = 0.001$ at 25°C. and 0.070 at 190°C. Gruver and Calvert originally attributed this rise in the quantum yield of methane at temperatures below 250°C. to the onset of reaction 1. However their picture cannot be correct, since propylene does not appear in the products until a temperature of 250°C. is reached.

As has been stated, evidence suggests that it is the α-methyl group which is lost in the decomposition of the excited aldehyde molecule. It is probable that the residual radical, $CH_3CH_2\dot{C}HCHO$, does not decompose to give propylene; it would more likely combine with other radicals at the low temperatures and decompose by reaction 10 to form additional methyl radicals at the higher temperatures.

$$CH_3CH_2\dot{C}HCHO \rightarrow CH_3\cdot + CH_2{=}CHCHO \qquad (10)$$

Thus the rate of propylene formation should be a truer measure of reaction 1 than the rate of methane formation. Gruver and Calvert did not use the yields of propylene, as they were thought to be anomalously low compared to the yields of methane and the accuracy of the analysis for this product was considered much less than that for methane.

In terms of the proposed mechanism there is considerable uncertainty in the value to be used for ϕ_{II} in the function 9. The most serious errors will result in the low-temperature data, where Φ_{CH_4} is small and the difference $(\Phi_{CH_4} - \phi_{II})$ is most subject to change in ϕ_{II}. The effect of using the data at relatively low temperatures and of choosing the value of 0.04 for ϕ_{II}, as Gruver and Calvert have done, is to lower the apparent activation energy which the data yield. Since it is not clear just what value should be chosen for ϕ_{II}, it is best to avoid the low-temperature rate data for methane in the evaluation of k_1. For the high-temperature data Φ_{CH_4} is large and the difference $(\Phi_{CH_4} - \phi_{II})$ is insensitive to the choice of this value.

The author has recalculated the data of Gruver and Calvert, estimating ϕ_{II} by an extrapolation of the low-temperature rates of methane formation. Only the reliable methane data in runs above 250°C. have been used. Also, the rate constant ratio $k_1/k_6^{1/2}$ was calculated from the rate data for propylene at all temperatures, using function 11.

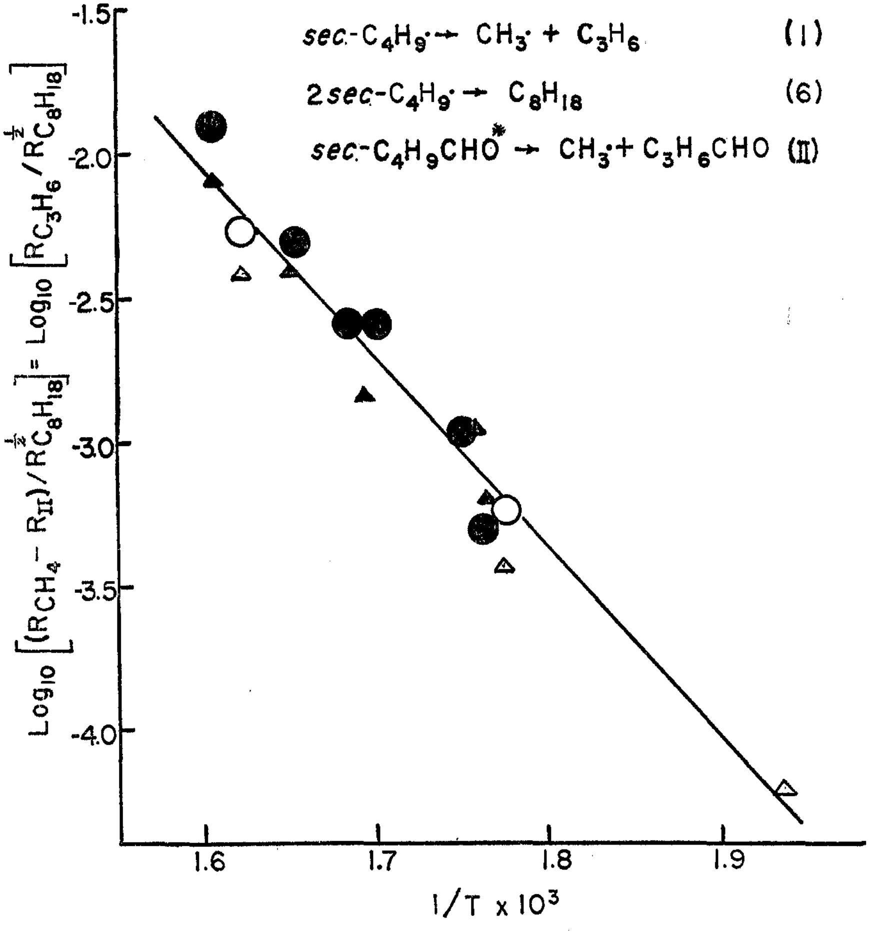

FIG. 2. Arrhenius plot of the rate functions theoretically equal to $k_1/k_6^{1/2}$ recalculated from the data of Gruver and Calvert (12) as described in the text. Rate data for methane are shown as circles, data for propylene as triangles; the darkened symbols are from photolyses of 2-methylbutanal at 3130 A.; the open symbols are from full-mercury-arc photolyses (ninetyfold increase in absorbed light intensity); the units of the rate functions are (mole/l.-sec.)$^{1/2}$.

$$\frac{\Phi_{C_3H_6}I_a^{1/2}}{(\Phi_{C_8H_{18}})^{1/2}} = k_1/k_6^{1/2} \tag{11}$$

The general compatibility of the different estimates is evident in the Arrhenius plot of the data shown in figure 2. Data for methane are shown as circles, and data for propylene as triangles. The darkened symbols are from experiments at 3130 A.; the open symbols are from full-arc runs. The scatter of the data reflects the inherent inaccuracies in the analysis for the minor products, methane, propylene, and octane, but the data based on propylene and methane are entirely consistent. A least-squares treatment of these data gives:

$$k_1/k_6^{1/2} = 4.53 \times 10^8 e^{-30.6/RT} \text{ (mole/cc.-sec.)}^{1/2}$$

If one assumes $k_6 = k_{12} = 2.2 \times 10^{13}$ cc./mole-sec. (17), k_1 can be estimated:

$$2CH_3\cdot \rightarrow C_2H_6 \tag{12}$$

$$k_1 \cong 2.1 \times 10^{15} e^{-30.6/RT} \text{ sec.}^{-1}$$

Similarly, from Mandelcorn and Steacie's value of $k_{-1}/k_{12}^{1/2}$ it is found that:

$$k_{-1} \cong 6.0 \times 10^{10} e^{-6.0/RT} \text{ cc./mole-sec.}$$

Thus it is estimated that $\Delta H_1 \cong E_1 - E_{-1} = 30.6 - 6.0 = 24.6$ kcal./mole, a value in good agreement with thermal estimates of $\Delta H_1 \cong 22$–25 kcal./mole. The ratio of the preëxponential factors of the rate constant for the forward and reverse of reaction 1 is off by a factor of 30 from that expected theoretically from the estimated entropy change of the reaction. This may be expected, since the data are not highly accurate. However, the revised photochemical kinetic estimate of k_1 is in sufficiently good agreement with thermal data to reaffirm faith in the thermal estimates of ΔH_1 and to establish the inaccuracy of the "low" kinetic estimates of E_1.

III. THE DECOMPOSITION REACTION OF THE *n*-PROPYL RADICAL

$$n\text{-}C_3H_7\cdot \rightarrow CH_3\cdot + C_2H_4 \tag{2}$$

The incompatibility of the published kinetic data and the thermal data for reaction 2 is even more marked than that for the decomposition reaction of the *sec*-butyl free radical which has been described. There are three independent determinations from photochemical and thermal kinetic experiments which suggest $E_2 \cong 19$–21 kcal./mole (7, 10, 15). Reasonable thermal data suggest $\Delta H_2 \cong 23$–26 kcal./mole. Mandelcorn and Steacie (14) report that $E_{-2} \cong 7$ kcal./mole. A more recent detailed study of Brinton (4) gives $E_{-2} \cong 8.7$ kcal./mole. Thus kinetic data suggest that $\Delta H_2 \cong E_2 - E_{-2} = 10$–$12$ kcal./mole. Obviously the reliability of the estimates of E_2 may be questioned.

A. PUBLISHED KINETIC ESTIMATES OF THE RATE OF DECOMPOSITION OF THE *n*-PROPYL RADICAL

The author is aware of only a preliminary note describing the first published study of reaction 2 (10). No data have been given, so the evaluation of the accuracy of the estimate, $E_2 \cong 19$ kcal./mole, is impossible.

The second study of this reaction involved the mercury-photosensitized decomposition of propane (7). The technique of Bywater and Steacie was the same as that which they used in the study of *n*-butane discussed earlier. This system has the same difficulties, and the chances for error in the estimate of E_2 are high.

Masson (15) has derived an estimate of k_2 from a quantitative study of the photolysis of di-*n*-propyl ketone at 3130 A. Only that part of the photolysis mechanism which concerns the estimates of k_2 need be considered here.

$$(n\text{-}C_3H_7)_2CO + h\nu \rightarrow n\text{-}C_3H_7\cdot + n\text{-}C_3H_7\dot{C}O \tag{III}$$

$$(n\text{-}C_3H_7)_2CO + h\nu \rightarrow C_2H_4 + n\text{-}C_3H_7COCH_3 \tag{IV}$$

$$n\text{-}C_3H_7\cdot \rightarrow C_2H_4 + CH_3\cdot \tag{2}$$

$$2n\text{-}C_3H_7\cdot \rightarrow n\text{-}C_6H_{14} \tag{13}$$

$$n\text{-}C_3H_7\cdot + CH_3\cdot \rightarrow n\text{-}C_4H_{10} \tag{14}$$

$$2CH_3\cdot \rightarrow C_2H_6 \tag{12}$$

$$CH_3\cdot + (n\text{-}C_3H_7)_2CO \rightarrow CH_4 + \cdot C_3H_6COC_3H_7 \tag{15}$$

$$n\text{-}C_3H_7\cdot + (n\text{-}C_3H_7)_2CO \rightarrow C_6H_{14} + n\text{-}C_3H_7\dot{C}O \tag{16}$$

The data from this study appear to be very reliable and self-consistent; e.g., at the higher temperatures where reaction 2 becomes measurable, the relationship between the products ethylene, methane, ethane, and butane, which is theoretically expected from the proposed mechanism, is followed closely.

$$\Phi_{C_2H_4} - \phi_{IV} = \Phi_{CH_4} + 2\Phi_{C_2H_6} + \Phi_{C_4H_{10}}$$

$\Phi_{C_2H_4}$ represents the total quantum yield of ethylene formation; ϕ_{IV} is the yield of ethylene from primary process IV, as estimated from the data for 161°C. and below.

Masson uses two methods to estimate k_2. Both of them depend ultimately on the rate function 17.

$$\frac{(\Phi_{C_2H_4} - \phi_{IV})I_a^{1/2}}{(\Phi_{C_6H_{14}} - \Phi'_{C_6H_{14}})^{1/2}} = \frac{k_2}{k_{13}^{1/2}} \tag{17}$$

Hexane is formed in two reactions in this system, so that the quantum yield of that formed in reaction 16, $\Phi'_{C_6H_{14}}$, must be subtracted from the measured quantum yield of hexane. An accurate estimate of $\Phi'_{C_6H_{14}}$ is difficult, since an extrapolation of the low-temperature rate data is required. From the temperature dependence of function 17 Masson finds $E_2 - E_{13}/2 \cong 20 \pm 1$ kcal./mole. The unusual complications encountered make this system poorly suited for the accurate estimation of k_2, and the value derived for E_2 may be considerably in error. It has been pointed out to the author that an error of 12 per cent in the value of the denominator of rate function 17, a reasonable error in view of the complications, would bring the Masson data into line with the thermal data for reaction 2.

It is possible that a complication similar to that suggested in the study of 2-methylbutanal is also present here. Masson finds that only one-half of the light-absorbing molecules of di-*n*-propyl ketone decompose up to 161°C.; presumably the other half are involved in deactivation processes. The occurrence of primary process IV has been demonstrated unambiguously; nevertheless at temperatures above 161°C. a portion of the methyl-containing products and ethylene attributed to reaction 2 may be derived from the decomposition of some of the large number of absorbing ketone molecules which may lose their electronic excitation by internal conversion in the fashion which is suggested for 2-methylbutanal. Such a hypothesis for *ketone* molecules has no direct support or refutation from experimental data now available to the author. However, in view of the probable occurrence of this complicating reaction in the aldehydes, it may be desirable to consider and evaluate this hypothesis in future studies of other systems in which the primary quantum yield of photodecomposition is significantly less than unity.

It is clear that no great confidence can be placed in any of the three kinetic estimates of E_2. A consideration of two independent investigations of reaction 2 which have been made recently will be instructive. They were designed to minimize many of the difficulties of the previous studies, and their results bring the kinetic data for reaction 2 in line with thermal data.

B. RECENT REDETERMINATIONS OF THE RATE OF DECOMPOSITION OF THE *n*-PROPYL RADICAL

1. High-temperature photolysis of butyraldehyde

Trotman-Dickenson and Kerr (18) are studying the high-temperature full-arc photolysis of butyraldehyde. Under their conditions the mechanism of the photolysis should be described adequately by the following:

$$n\text{-C}_3\text{H}_7\text{CHO} + h\nu \rightarrow n\text{-C}_3\text{H}_7\cdot + \dot{\text{C}}\text{HO} \tag{V}$$

$$n\text{-C}_3\text{H}_7\text{CHO} + h\nu \rightarrow \text{C}_2\text{H}_4 + \text{CH}_3\text{CHO} \tag{VI}$$

$$n\text{-C}_3\text{H}_7\cdot \rightarrow \text{C}_2\text{H}_4 + \text{CH}_3\cdot \tag{2}$$

$$n\text{-C}_3\text{H}_7\cdot + n\text{-C}_3\text{H}_7\text{CHO} \rightarrow \text{C}_3\text{H}_8 + n\text{-C}_3\text{H}_7\dot{\text{C}}\text{O} \tag{18}$$

$$\text{CH}_3\cdot + n\text{-C}_3\text{H}_7\text{CHO} \rightarrow \text{CH}_4 + n\text{-C}_3\text{H}_7\dot{\text{C}}\text{O} \tag{19}$$

$$n\text{-C}_3\text{H}_7\dot{\text{C}}\text{O} \rightarrow n\text{-C}_3\text{H}_7\cdot + \text{CO} \tag{20}$$

$$2n\text{-C}_3\text{H}_7\cdot \rightarrow n\text{-C}_6\text{H}_{14} \tag{13}$$

When the chains are long and the yield of ethylene from reaction VI is small compared to that from reaction 2, then the mechanism suggests:

$$R_{\text{CH}_4}/R^{1/2}_{\text{C}_6\text{H}_{14}} = R_{\text{C}_2\text{H}_4}/R^{1/2}_{\text{C}_6\text{H}_{14}} = k_2/k^{1/2}_{13}$$

The preliminary results from the methane rate function (nearly equal to that found for the ethylene function) give

$$k_2/k^{1/2}_{13} = 6.6 \times 10^4 e^{-25.4/RT}\ (\text{mole/cc.-sec.})^{1/2}$$

Thus Trotman-Dickenson and Kerr estimate $E_2 - E_{13}/2 \cong 25.4$ kcal./mole. Since most of the *n*-propyl radicals which undergo reaction 2 will have been generated in the thermal chain sequence 18 and 20, this result should be uncomplicated by many of the possible difficulties which were encountered in the earlier work and should be more reliable.

2. The sensitized decomposition of butyraldehyde

The author has recently completed a study of reaction 2 which is believed to avoid the problems usually encountered in photochemical studies of decomposition reactions (9). The thermal decomposition of butyraldehyde has been sensitized through the selective photolysis of azomethane at 3660 A. Purely thermal *n*-propyl radicals are generated homogeneously under these conditions. The following are the dominant reactions in this system:

$$CH_3N_2CH_3 + h\nu \rightarrow 2CH_3\cdot + N_2 \tag{VII}$$

$$CH_3\cdot + n\text{-}C_3H_7CHO \rightarrow CH_4 + n\text{-}C_3H_7\dot{C}O \tag{19}$$

$$n\text{-}C_3H_7\dot{C}O \rightarrow n\text{-}C_3H_7\cdot + CO \tag{20}$$

$$n\text{-}C_3H_7\cdot + n\text{-}C_3H_7CHO \rightarrow C_3H_8 + n\text{-}C_3H_7\dot{C}O \tag{18}$$

$$n\text{-}C_3H_7\cdot \rightarrow C_2H_4 + CH_3\cdot \tag{2}$$

$$n\text{-}C_3H_7\cdot + CH_3\cdot \rightarrow n\text{-}C_4H_{10} \tag{14}$$

$$2CH_3\cdot \rightarrow C_2H_6 \tag{12}$$

From the temperature dependence of the rate function 21,

$$\frac{R_{C_2H_4}R_{C_2H_6}^{1/2}}{R_{C_4H_{10}}} = \frac{k_2\,k_{12}^{1/2}}{k_{14}} \tag{21}$$

the following relation is derived:

$$k_2k_{12}^{1/2}/k_{14} = 10^{8.783}e^{-34.9/RT}\ (\text{mole/cc.-sec.})^{1/2}$$

If one assumes $k_{12} = k_{14} = 2.2 \times 10^{13}$ cc./mole-sec. (17), then it is estimated that

$$k_2 \cong 2.8_5 \times 10^{15}e^{-34.9/RT}\ \text{sec.}^{-1}$$

Brinton recently estimated the rate of addition of methyl to ethylene. He finds:

$$k_{-2}/k_{12}^{1/2} = 3.3 \times 10^{-7}e^{-8.66/RT}\ (\text{cc./molec.-sec.})^{1/2}$$

Changing the units to moles-cc.-sec. and using Shepp's value for k_{12},

$$k_{-2} \cong 1.20 \times 10^{12}e^{-8.66/RT}\ (\text{cc./mole-sec.})$$

The rate constants for the forward reaction 2 and its reverse appear to be reasonably consistent. The data suggest $\Delta H_2 \cong 26.2$ kcal./mole and $\Delta S_2^\circ = R \ln (A_2/A_{-2}) \cong 15.4$ e.u. (standard state, 1 mole/cc.). These estimates check well with the values of $\Delta H_2 = 26.4$ and $\Delta S_2^\circ = 12.1$ e.u., calculated from Bryant's summary of thermal data and his theoretical estimates of the entropy of the *n*-propyl and methyl radicals (5). The observed difference in the experimental and theoretical values for ΔS_2° corresponds to a factor of 5.3 in the A_2/A_{-2} ratio or about 1.7 kcal./mole in the difference in activation energies, $E_2 - E_{-2}$; thus the divergence from "theory" is well within the experimental error and the simplifications involved in this comparison.

IV. CONCLUSION

It has been seen that enthalpy data derived from different sources for certain organic free radicals, e.g., *sec*-$C_4H_9\cdot$, *n*-$C_3H_7\cdot$, $H\dot{C}O$, and $CH_3\dot{C}O$, are in striking disagreement; data based on photochemical kinetic estimates are significantly different from those derived from electron-impact and "reasonable" thermal data. A reëvaluation has been made of the kinetic data related to two of the reactions about which much confusion exists:

$$sec\text{-}C_4H_9\cdot \rightarrow CH_3\cdot + C_3H_6 \tag{1}$$

$$n\text{-}C_3H_7\cdot \rightarrow CH_3\cdot + C_2H_4 \tag{2}$$

The study has shown that the "down-chain" splits observed in the photolysis of many aldehyde and ketone molecules, previously attributed to a primary process, probably occur during the process of internal conversion and degradation of electronic energy contained in the molecule. It is likely that this rather unexpected source of molecular fragmentation has led to significant error in many of the photochemical kinetic estimates of the rate constants for the decomposition of free radicals. A reconsideration of the data for reaction 1 in terms of this mechanism has eliminated the apparent conflict of kinetic and thermal data concerning this reaction. New kinetic data have confirmed the reliability of the thermal data for reaction 2 also.

It is concluded that extreme caution must be exercised to recognize and correct for possible complications in the determination of rates of decomposition of free radicals with the conventional photochemical systems. In future kinetic studies of the decomposition reactions of radicals it is recommended that the generation of thermally equilibrated free radicals (R· or RCO·) be accomplished through the selective photolysis of azomethane in mixtures with the necessary aldehyde (RCHO). Most of the complications of the usual photochemical systems, e.g., "hot" radicals, molecular fragmentation following internal conversion, etc., are avoided, and many of the virtues of the photochemical techniques, such as homogeneous radical production, flexibility in the choice of temperature, etc., are retained.

V. REFERENCES

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