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## PHYSICAL AND INORGANIC CHEMISTRY

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, HAVERFORD COLLEGE, HAVERFORD, PENNSYLVANIA]

### The Mercury $6(^3P_1)$ Photosensitized Decomposition of Propane and 2,2-Dideuteriopropene

BY JOHN P. CHESICK

RECEIVED MARCH 9, 1964

Ethylene has been used as a hydrogen atom scavenger and the radical combination products have been determined for the resulting ethyl, isopropyl, and *n*-propyl radicals produced by the mercury-photosensitized (2537 Å.) decomposition of propane, 2,2-dideuteriopropene, and mixtures of these propanes. From the measurements of the radical combination products and values for the radical disproportionation-recombination ratios, the isopropyl-*n*-propyl product ratios from the dissociative quenching process have been determined for the two propanes. These ratios, 9.9 for  $C_3H_8$  and 0.55 for  $C_3H_6D_2$ , are shown to be in excellent agreement with the view that quenching of the excited mercury takes place through a specific transition state and that dissociation of the alkane ensues from this transition state *without* formation of another cyclic intermediate with the mercury atom prior to dissociation. This cyclic intermediate has been proposed previously based on the propyl product ratios obtained using a different scavenger system.

#### Introduction

The existence of a large isotope effect in the dissociative quenching of alkanes by Hg  $6(^3P_1)$  has been noted in our laboratory<sup>1</sup> as well as in others.<sup>2</sup> Rousseau and Gunning<sup>3</sup> have measured the mercury  $6(^3P_1)$  quenching cross sections,  $\sigma_Q^2$ , of a variety of hydrocarbons deuterated in various positions and have shown that deuteration causes substantial changes in the quenching cross sections of contributing groups in the molecules. The additivity of the square roots of group quenching cross sections had been suggested by Darwent<sup>4</sup> on examination of quenching cross sections for a wide variety of hydrocarbons. His quenching data and data from other sources for a variety of other molecules have been gathered and analyzed<sup>5</sup> to provide a fairly clear picture of Hg  $6(^3P_1)$  acting as an electrophilic reagent in the reaction through an attack on alkane C-H bonds *via* a linear transition state. However Gunning, *et al.*,<sup>2</sup> reported data for the photosensitized decomposition of propane which they analyzed to indicate approximately equal amounts of *n*-propyl and isopropyl radicals produced in the primary decomposition. This led them to postulate a five-membered cyclic species as an intermediate between the linear activated complex formed in the rate-determining attack by Hg  $6(^3P_1)$  and the final carbon-hydrogen bond rupture.

This sequence of events was represented<sup>2,5</sup> in the following manner where the rate-determining reaction is shown occurring at the secondary hydrogen.

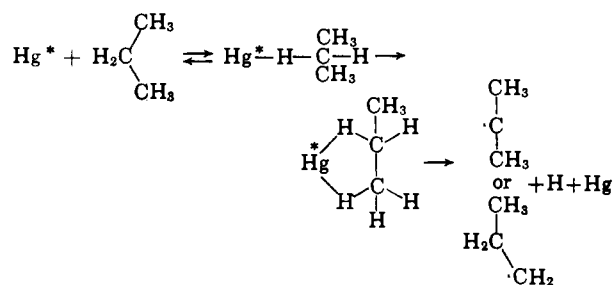
(1) J. P. Chesick, *J. Am. Chem. Soc.*, **84**, 2448 (1962).

(2) G. N. C. Woodall and H. E. Gunning, *Bull. soc. chim. Belges*, **71**, 725 (1962).

(3) Y. Rousseau and H. E. Gunning, *Can. J. Chem.*, **41**, 465 (1963).

(4) B. deB. Darwent, *J. Chem. Phys.*, **18**, 1532 (1950).

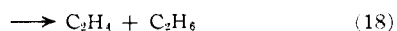
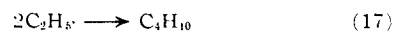
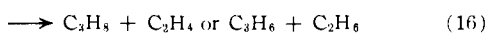
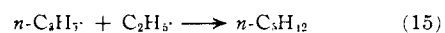
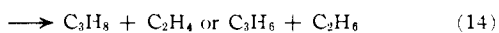
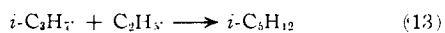
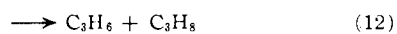
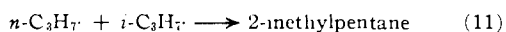
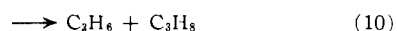
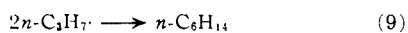
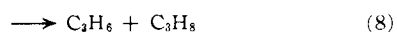
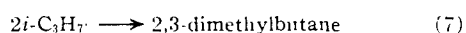
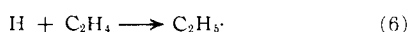
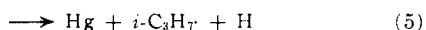
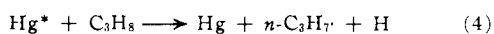
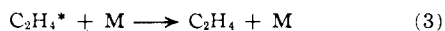
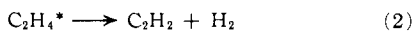
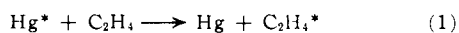
(5) Y. Rousseau, O. P. Strausz, and H. E. Gunning, *ibid.*, **39**, 962 (1963).



Holroyd<sup>6</sup> has recently published work describing the use of labeled ethylene as a hydrogen atom scavenger in the Hg  $6(^3P_1)$  photosensitized decompositions of propane, *n*-butane, isobutane, *n*-pentane, isopentane, and other saturated hydrocarbons. From the relative yields of certain radical recombination products, he deduced the relative amounts of primary and secondary C-H cleavage in the primary process. He obtained a ratio of 9:1 for isopropyl-*n*-propyl radical production from propane, in marked contrast to the 1:1 ratio reported by Gunning. We are here reporting our data for similar studies comparing the products of the Hg  $6(^3P_1)$  photosensitized decomposition of propane and 2,2-dideuteriopropene, also using ethylene as a hydrogen atom scavenger. These experiments were carried out independently of the work reported by Holroyd and provide what we believe to be valid information concerning the alkane decomposition isotope effect and a picture of the course of the quenching-decomposition process which disagrees with the one deduced by Gunning. Our experiments using propane included hexane analyses and provide data using higher ethylene-propane ratios and reactant pressures than those employed by Holroyd. Our data support his conclusions con-

(6) R. A. Holroyd and G. W. Klein, *J. Phys. Chem.*, **67**, 2273 (1963).

cerning the relative radical yields from the primary process for propane as well as provide added data for the one isotopically substituted propane. In the presence of sufficient ethylene to scavenge the hydrogen atoms produced in reactions 4 and 5, we believe that the following sequence describes the significant reactions occurring in our system. Here  $\text{Hg}^*$  represents the  $\text{Hg}(^3\text{P}_1)$  produced by the 2537-Å. resonance radiation. Hence, measurements of the pentanes and hexanes produced and reasonable values for the disproportionation recombination rate constant ratios currently available make possible the calculation of the



desired  $k_5/k_4$ . Butane analysis permits a check of the yield of ethyl radicals produced in reaction 6 against the total of reactions 4 and 5.

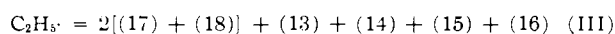
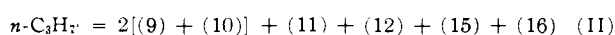
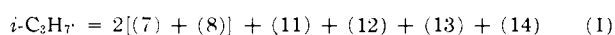
### Experimental

The apparatus and procedures were essentially those of the previously reported work<sup>1</sup> in the ethylene-propane-mercury system. A 3.6-cm. diameter and 25-cm. long quartz reaction vessel was irradiated with light from a Hanovia 88-A45 Vycor low pressure mercury resonance lamp. No significant amount of the I849 line was transmitted. A shutter permitted warm-up of the lamp prior to the photolysis. Gas mixtures were circulated through a trap at 0° and then through the photolysis cell by means of a Teflon-covered stirring bar which was magnetically rotated at high speed inside a closely fitting glass "pillbox" ported to serve as a centrifugal pump. The product mixture was transferred at low pressures through a stopcock greased with Kel-F perfluorinated grease to the g.l.p.c. sample trap for analysis after noncondensable product measurement. Grease-free valves were used in the photolysis cell system. The pressure and volume of product gases noncondensable in liquid nitrogen were measured after cycling this gas two or three times through a trap at liquid nitrogen temperature by means of a Toepler pump. Most of the runs were at temperatures between 29 and 32°. A 12-ft. gas chromatography column packed with GE SF-96 silicone oil on firebrick provided the principal product separation. A short length of a column of silver nitrate in glycerol on firebrick provided an additional separation of butene-1, propylene, and 3-methylbutene-1 from the saturated compounds. Operation with and without this additional section demonstrated that these were the only  $\text{C}_4$ - $\text{C}_6$  unsaturates present in observable quantities. All of the products reported appeared as well-resolved peaks except for 2-methylpentane which was not completely resolved from the 2,3-dimethylbutane. This could be estimated with a relative error of  $\pm 10$ - $15\%$  in most of the runs with the undeterated propane. The determination of this peak became

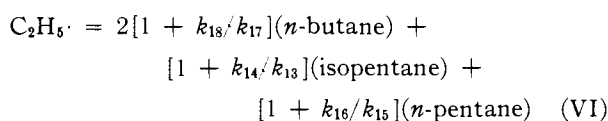
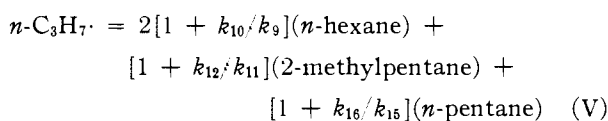
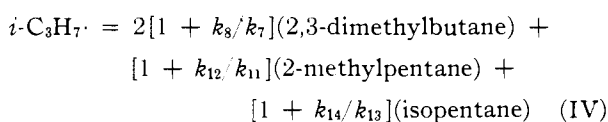
more precise in the case of runs with deuterated propane when the 2-methylpentane peak became of comparable size to the 2,3-dimethylbutane peak. The precision of measurement of the  $n$ -hexane peak varied between  $\pm 40$  and  $\pm 20\%$  due to its small size in the runs with undeterated propane. It was necessary to calibrate the g.l.p.c. detector, a Gow-Mac thermistor bridge, with measured amounts of reference compounds because of the varying detector sensitivity to the compounds of different molecular weight. Matheson research grade varieties of argon, ethylene, and propane were used. The 2,2-dideteriopropene of better than 98% isotopic purity was obtained from Merck of Canada.

### Results and Discussion

**Calculation of  $k_5/k_4$ .**—Assuming reactions 1-18 account for the observed products, material balances may be written for the fate of the  $i\text{-C}_3\text{H}_7$ ,  $n\text{-C}_3\text{H}_7$ , and  $\text{C}_2\text{H}_5$  radicals produced by reactions 4, 5, and 6 in terms of the contributions of each of the reactions 7-18. The supposition that this is a complete set of significant reactions will be discussed in detail later.



In terms of the stable recombination products which were measured and the disproportionation-recombination rate constant ratios, I, II, and III become



The following values of disproportionation-recombination rate constant ratios were used to evaluate IV, V, and VI for each run:  $k_8/k_7 = 0.6$ ,<sup>7,8</sup>  $k_{18}/k_{17} = 0.31$ ,<sup>9</sup>  $k_{14}/k_{13} = 0.40$ ,<sup>6,10</sup>  $k_{10}/k_9 = 0.13$ ,<sup>11</sup>  $k_{16}/k_{15} = 0.14$ .<sup>12</sup> It should be noted that there is some choice of values for  $k_{18}/k_{17}$ . Kerr and Trotman-Dickenson<sup>8</sup> prefer 0.15 as a considered general value. However, the value of 0.31 recently reported by Back was for  $\text{C}_2\text{H}_5$  produced by addition to ethylene of hydrogen atoms produced by mercury photosensitization. Use of the value 0.15 for  $k_{18}/k_{17}$  has the general effect of reducing the calculated total ethyl production (VI) by 6%. This somewhat improves the agreement between VI and IV + V in the cases where ethylene depletion is not significant.

$k_{14}/k_{13}$  is a sum of values for production of  $\text{C}_3\text{H}_8 + \text{C}_2\text{H}_4$ <sup>10</sup> and for production of  $\text{C}_3\text{H}_6 + \text{C}_2\text{H}_6$ .<sup>6</sup> The value used for  $k_{12}/k_{11}$  was an average of those taken for  $k_{10}/k_9$  and  $k_8/k_7$  since no numbers were found in the

(7) C. A. Heller and A. S. Gordon, *J. Phys. Chem.*, **60**, 1315 (1956).

(8) J. A. Kerr and A. F. Trotman-Dickenson, *Progr. Reaction Kinetics*, **1**, 111 (1961).

(9) R. A. Back, *Can. J. Chem.*, **37**, 1834 (1959).

(10) J. A. G. Domingues, J. A. Kerr, and A. F. Trotman-Dickenson, *J. Chem. Soc.*, 3357 (1962).

(11) S. G. Whiteley and C. R. Masson, *J. Chem. Phys.*, **25**, 233 (1956).

(12) R. A. Holroyd and T. E. Pierce, 146th National Meeting of the American Chemical Society, Denver, Colo., Jan. 20, 1963; *J. Phys. Chem.*, to be published.

TABLE I  
 PRODUCT YIELDS,  $10^3 \times$  AMOUNTS RELATIVE TO PROPANE

Run no.	C <sub>3</sub> H <sub>8</sub> /C <sub>3</sub>	Propane P, mm.	H <sub>2</sub>	n-C <sub>3</sub> H <sub>10</sub>	i-C <sub>3</sub> H <sub>12</sub>	n-C <sub>4</sub> H <sub>12</sub>	2,3-Dimethylbutane	2-Methylpentane	n-C <sub>5</sub> H <sub>14</sub>	IV + V	VI	k <sub>5</sub> /k <sub>4</sub>
21	0.134	46	4.45	1.39	1.75	0.25	0.71	...	...	e	e	e
28	0.063	8.4	17.1	3.04	4.73	0.90	2.96	0.71	0.059	19.4	15.6	7.7
25	0.091	8.0	15.2	1.98	2.68	0.36	1.02	0.26	≤0.03	8.2	9.3	8.4
29	0.070	9.1 <sup>a</sup>	...	2.25	3.81	0.49	1.55	0.28	...	11.7	11.7	10.9
27	0.075	44	1.13	1.15	1.56	0.235	0.64	0.12	0.002	4.8	5.5	10.0
32	0.080	44	2.2	0.98	1.42	0.191	0.58	0.10	0.011	4.4	4.5	10.2
30	0.079	45 <sup>b</sup>	...	0.98	1.42	0.184	0.53	0.11	0.006	4.2	4.8	10.0
39	0.081	43	1.51	0.60	0.86	0.116	0.34	0.095	0.015	2.75	2.70	8.0
26	0.070	138	...	0.76	1.06	0.134	0.46	0.069	0.005	3.3	3.6	11.4
17	0.038	48	...	2.8	4.76	0.63	2.33	0.46	0.035	16.3	14.7	9.9
18	0.044	43	3.2	2.1	3.16	0.44	1.54	0.26	0.036	10.6	10.5	10.6
19	0.050	46	4.5	2.97	4.58	0.65	2.29	0.27	0.043	15.4	14.9	11.4
40	0.036	42	1.32	0.83	1.17	0.14	0.50	0.13	0.008	3.8	3.8	9.4
20	0.012	42	5.1	1.15	3.82	0.46	4.13	0.50	0.059	20.7	8.9	13.8
36	0.012	48	4.7	1.49	4.02	0.49	3.81	0.73	0.056	20.0	10.1	10.6
22	0.012	45	2.6	1.14	2.79	0.38	2.02	0.36	...	11.9	7.3	11.2
37	0.014	42	2.2	1.08	2.47	0.28	1.55	0.28	0.024	9.6	6.6	11.2
23	0	48	6.8	...	...	...	4.66	0.53	0.065	...	...	...
33	0.064	49	2.3	0.56	0.78	0.28	0.31	0.059	0.026	2.64	2.87	4.61
		64% C <sub>3</sub> H <sub>8</sub> D <sub>2</sub>										
35	0.014	44	2.9	1.49	2.63	0.78	1.58	0.66	0.109	11.9	8.5	4.57
		60% C <sub>3</sub> H <sub>8</sub> D <sub>2</sub>										
38	0.012	44	1.47	0.84	1.29	0.38	0.57	0.29	0.054	5.1	4.4	4.12
		62% C <sub>3</sub> H <sub>8</sub> D <sub>2</sub>										
42	0.035	46	2.3	0.57	0.56	0.36	0.157	0.18	0.049	2.35	2.59	1.98
		83% C <sub>3</sub> H <sub>8</sub> D <sub>2</sub>										
31	0.080	43 <sup>c</sup>	3.2	0.33	0.116	0.30	0.013	0.043	0.054	0.79	1.05	0.51
34	0.014	46 <sup>c</sup>	2.0	0.78	0.50	0.98	0.058	0.344	0.304	3.7	3.9	0.61
41	0.036	46 <sup>c</sup>	1.43	0.22	0.093	0.236	0.012	0.057	0.061	0.75	0.73	0.52
24	47 mm. C <sub>2</sub> H <sub>4</sub> only		8.3	0.128 <sup>d</sup>	...	...	...	...	...	...	...	...

<sup>a</sup> 201 mm. Ar added. <sup>b</sup> 203 mm. Ar added. <sup>c</sup> C<sub>3</sub>H<sub>8</sub>D<sub>2</sub>. <sup>d</sup> Relative to C<sub>2</sub>H<sub>4</sub>  $\times 10^3$ ; no products heavier than C<sub>4</sub> were seen. <sup>e</sup> G.l.p.c. analysis failed after the 2,3-dimethylbutane peak; relative amounts of products through this peak were virtually identical with analysis of run 27.

literature for this ratio; it seems highly unlikely that  $k_{12}/k_{11}$  should lie outside of the range spanned by  $k_{10}/k_9$  and  $k_8/k_7$ . It should be noted finally that these ratios were chosen before computation of values for IV, V, and VI and hence were not used as "adjustable parameters."

The ratio of isopropyl-*n*-propyl radicals produced by reactions 5 and 4,  $k_5/k_4$ , is then taken to be the value of IV/V for each run and is tabulated in Table I. All products, as well as the computed quantities IV, V, and VI, are presented as  $10^3$  times the ratio of the product to propane. The times for the runs were ca. 45 sec., with a variation of a factor of three. Inefficiency of the circulation pump and resulting unevenness in the mercury concentration in the photolysis cell caused somewhat variable photolysis rates; therefore, times were not included with the data of Table I. There was in general a much reduced rate of reaction in the runs with the deuterated propane; cf Table II and later discussion.

**Effects of Quenching by Radical Scavengers.**—A serious criticism of the use of nitric oxide as a radical trap is that 2% nitric oxide in propane causes 28% of the quenching of Hg 6(<sup>3</sup>P<sub>1</sub>) atoms, taking  $\sigma_Q^2$  for propane as  $1.3 (\text{Å}^2)^4$  and the value of  $25 (\text{Å}^2)^{13}$  for  $\sigma_Q^2$  of nitric oxide. Strausz and Gunning<sup>14</sup> have recently described in detail the complex decomposition reactions of alkanes initiated at room temperature by the excited

C <sub>3</sub> H <sub>8</sub> /C <sub>3</sub>	$x_Q(\text{C}_2\text{H}_4)^d$	$R_{19}/(R_{19} + R_8)^b$
2.0 <sup>f</sup>	0.97	0.001
0.134	0.71	0.014
0.080	0.60	0.023
0.036	0.40	0.050
0.0135	0.20	0.12
0.0026 <sup>d</sup>	0.05	0.42
0.064 <sup>e</sup>	0.63	
0.036 <sup>f</sup>	0.84	
0.035 <sup>g</sup>	0.64	

<sup>a</sup> Fraction of Hg 6(<sup>3</sup>P<sub>1</sub>) quenched by C<sub>2</sub>H<sub>4</sub>. <sup>b</sup> Fraction of hydrogen atoms produced which undergo abstraction reaction. <sup>c</sup> Typical of previously reported work.<sup>1</sup> <sup>d</sup> Largest ratio employed by Holroyd in propane experiments.<sup>6</sup> <sup>e</sup> 64% C<sub>3</sub>H<sub>8</sub>D<sub>2</sub> in propane mixture. <sup>f</sup> C<sub>3</sub>H<sub>8</sub>D<sub>2</sub>. <sup>g</sup> 83% C<sub>3</sub>H<sub>8</sub>D<sub>2</sub> in propane mixture.

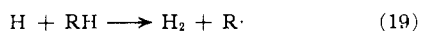
nitric oxide produced on the quenching of Hg 6(<sup>3</sup>P<sub>1</sub>), i.e.,  $\text{Hg}^* + \text{NO} \rightarrow \text{NO}^*(^4\pi) + \text{Hg}$ .  $\text{NO}^* + \text{RH} \rightarrow$  a plethora of products. They found the quantum yield of nitrogen to be 0.42 on irradiating a mixture of 233 mm. nitric oxide and 26 mm. propane; for this ratio essentially all of the mercury quenching is by nitric oxide. A quantum yield of 0.04 was reported for condensable products, leaving the fate of the bulk of the oxygen atoms in doubt; for the C<sub>3</sub>-containing species identified, the ratio *n*-propyl-isopropyl was 0.8(i). Hence it may be suspected that the products of the more than 28% of the mercury excitation which acted on the propane via the nitric oxide reactions in the work with NO present as 2% or more as a "radical trap"<sup>12</sup> affect the

(13) J. R. Bates, *J. Am. Chem. Soc.*, **52**, 3925 (1930); **54**, 569 (1932).

(14) O. P. Strausz and H. E. Gunning, *Can. J. Chem.*, **41**, 1207 (1963).

isopropyl-*n*-propyl product ratio. This is the ratio attributed solely to the interaction of Hg 6(<sup>3</sup>P<sub>1</sub>) with propane.<sup>2</sup> It is therefore most important to scrutinize with care the chemical effects of the energy transferred to ethylene in the work using this substance as a hydrogen atom scavenger.

Table II lists the fraction of Hg 6(<sup>3</sup>P<sub>1</sub>) quenching by ethylene in mixtures of varying ethylene-propane ratios as well as the fraction of hydrogen atoms which will form propyl radicals by abstraction from propane.

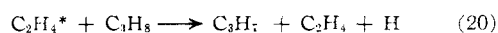


This fraction in terms of the rates  $R_{19}$  and  $R_6$  is

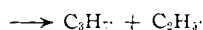
$$R_{19}/(R_{19} + R_6) = 1/[1 + (\text{C}_2\text{H}_4)k_6/(\text{C}_3\text{H}_8)k_{19}]$$

Holroyd<sup>6</sup> found  $k_{19}/k_6$  to be  $1.9 \times 10^{-3}$  for RH = propane, and 3.7, 3.7, and  $1.8 \times 10^{-3}$  for abstraction from pentane, hexane, and neohexane rather than propane. This was in agreement with the value for  $k_{19}/k_6$  for RH = butane of  $2.2 \times 10^{-3}$  calculated by Holroyd from recent data of Cvetanović<sup>15</sup> and Yang.<sup>16</sup> Back<sup>9</sup> found  $0.67 \times 10^{-3}$  as the ratio of rate constants for the two hydrogen atom reactions, abstraction from propane and addition to propylene. The ratio of rate constants for hydrogen atom addition to ethylene and for addition to propylene of 4.2<sup>17</sup> and Back's data give a value of  $2.8 \times 10^{-3}$  for  $k_{19}/k_6$ , also in good agreement with Holroyd's value. Knowing  $k_{19}/k_6$ , we are able to be safe in predictions concerning the relative unimportance of reaction 19.

Run 24 with ethylene alone at 47 mm. and at an irradiation time comparable to that of the bulk of the runs (50 sec.) showed only a minor amount of butane and a lesser amount of butene-1 in addition to the molecular hydrogen expected from reaction 2. Holroyd<sup>6</sup> obtained  $k_5/k_4$  by an extrapolation procedure to account for reaction 19, which was significant at the lower ethylene-propane ratios employed in his work. Quenching by excited ethylene, however, was not significant in his studies. Using larger proportions of ethylene in the work reported here, we effectively eliminate the hydrogen abstraction reactions without resort to extrapolation procedures, but we have a much larger fraction of the total quenching by ethylene. Reaction 1 is important, and we must concern ourselves by analogy with the reactions of NO\* with the possibility of excited ethylene-induced decomposition of propane.



or



Variation in the fractional quenching by ethylene (Table II) from less than 0.047 to 0.6 or 0.7, characteristic of the higher ethylene contents, has caused no systematic increase or significant change in the values of  $k_5/k_4$ . An even grosser test for the importance of reaction 20 is found in examination of the total product yields of previous work<sup>3</sup> at ethylene-propane ratios of ca. 2. In a typical experiment using similar procedures to those of the current work, 12 mm. of propane + 24 mm. of ethylene, irradiated for a period a hundred times longer than usually employed in the current

(15) M. Takahashi and R. J. Cvetanović, *Can. J. Chem.*, **40**, 1037 (1962).

(16) K. Yang, *J. Am. Chem. Soc.*, **84**, 3795 (1962).

(17) A. F. Trolman-Dickenson, "Gas Kinetics," Butterworth's Scientific Publications, London, 1955, p. 287.

study, gave the following product yields, expressed as per cent of the reactant propane: *n*-butane, 3.0; isopentane, 0.74; *n*-pentane, 0.145. The butane is formed from ethyl radicals by processes previously discussed. Secondary reactions in the ethylene system will lead to hexanes, but the pentanes probably arise from propyl-ethyl combination. In any event, the rate of pentane formation was approximately 1/100 of that found in the work being reported here, as might be expected from the small fraction of quenching by propane if reaction 20 is unimportant. Thus increasing the proportion of ethylene only becomes deleterious in studying the alkane decompositions at large C<sub>2</sub>H<sub>4</sub>-RH ratios when the products of reactions 4 and 5 are reduced to levels comparable to the extent of the secondary decomposition reactions resulting from reaction 1 and 2.

**Other Factors in Reaction Scheme.**—Addition of argon (runs 29, 30) caused no appreciable change in the product yields; diffusion to the walls is not influencing the nature of the radical species present.

The C<sub>2</sub>H<sub>5</sub>· and C<sub>3</sub>H<sub>7</sub>· material balance checks quite well, considering the latitude in a few of the disproportionation-recombination rate constant ratios. Exceptions are runs such as 28, 19, 20, 36, 22, and to a lesser extent 37 where there was an appreciable fraction of ethylene consumed and reaction 19 becomes apparent. The yield of hydrogen fits well that expected from reaction 2 except for the excess attributable to the abstraction process in the runs with marked ethylene depletion.

Holroyd<sup>6</sup> has eliminated the necessity for consideration of the abstraction reaction *n*-C<sub>3</sub>H<sub>7</sub>· + C<sub>3</sub>H<sub>8</sub> → C<sub>3</sub>H<sub>8</sub> + *i*-C<sub>3</sub>H<sub>7</sub>·.

Isomerization of hot propyl radicals, at least for the case involving deuterium migration, has been eliminated previously by the observation<sup>1</sup> that the isopentane is monodeuterated and the *n*-pentane is dideuterated if 2,2-dideuteriopropene is used.

Loss of alkyl radicals by addition to ethylene to form behavior radicals is unimportant as evidenced by the low yield of butene-1, pentene-1, and 3-methylbutene-1 which would be disproportionation products of such radical adducts. There also appears to be little effect of variation of total pressure by a factor of 17 at a constant light intensity. It is concluded from these arguments and others presented in the similar work<sup>6</sup> that reactions 1-18 are sufficient to describe our system.

**Conclusions Concerning Dissociative Quenching.**—Averaging the data for the runs with 100% C<sub>3</sub>H<sub>5</sub>D<sub>2</sub> and 100% C<sub>3</sub>H<sub>8</sub> and omitting the runs for which scavenger depletion may be significant, we obtain values of  $k_{5D}/k_4 = 0.55$ ,  $\alpha_D = 0.355$ ; and  $k_{5H}/k_4 = 9.87$ ,  $\alpha_H = 0.908$ , for the deuterated and undeuterated propanes. Here  $\alpha$  denotes the fraction of propane decomposition to isopropyl radicals, or  $k_5/(k_4 + k_5)$ . The value for  $k_{5H}/k_4$  is quite close to the value obtained by Holroyd using different data analysis and reactant mixtures. Woodall and Gunning reported<sup>2</sup>  $\alpha_D = 0.18$ ; we disagree with this value.

Holroyd defined and calculated an effective cross section per bond for quenching with dissociation for the various types of bonds in the alkanes he studied. The relative reactivities per bond were generally rather close to the relative quenching cross sections per bond calculated by Darwent solely from total molecular

quenching cross-section data. We can perform the same calculation using the product distribution data for our two isotopically substituted propanes, and the quenching cross sections measured by Rousseau and Gunning<sup>3</sup> for these two propanes.

Table III lists the dissociative quenching bond cross section for a bond of type  $i$  defined as before.<sup>6</sup> The

$$\sigma_{Q_i}/(\text{C-H})_i \text{ bond} = \sigma_{Q_i}\alpha_i/\text{number of } (\text{C-H})_i \text{ bonds}$$

quenching cross sections obtained for both propanes by Rousseau and Gunning<sup>3</sup> were used for internal consistency. The primary bond cross section calculated assuming dissociation occurs concomitantly with the quenching process at the particular bond is constant for the two propanes, and the ratio of the secondary bond cross sections for hydrogen and deuterium, 18.2, is essentially the same as the ratio  $(k_{5H}/k_4)/(k_{5D}/k_4) = 17.9$  found in this work. The data from the irradiation of the propane-dideuteriopropene mixtures can be analyzed for consistency with the preceding conclusions and reaction scheme. If dissociation occurs on quenching at a particular group or bond, the sum of the secondary bond dissociative quenching cross sections weighted by the mole fraction of each isotopic species in the mixture and divided by the corresponding weighted sum for the primary bonds should give the ratio of isopropyl- $n$ -propyl radicals in a mixture of a particular isotopic composition. Using the values from Table III, we calculate isopropyl/ $n$ -propyl ratios of 3.90 and 2.16 expected for mixtures containing 36.0 and 17.3%  $\text{C}_3\text{H}_8$  in the  $\text{C}_3\text{H}_8$ - $\text{C}_3\text{H}_6\text{D}_2$  mixture. These ratios are satisfactorily close to the average from runs 33, 35, and 38 of 4.43, and the value for run 42 of 1.98. Thus we agree with Gunning that the energy-transfer process takes place through the formation of an activated complex of a rather definite configuration, but we must conclude that the alkane dissociation occurs through this same complex as a result of the energy-transfer process without formation of some other intermediate prior to dissociation.

TABLE III

Hydrocarbon	$\sigma_{Q_i}, \text{Å}^2$	Secondary $\alpha$	$\sigma_{Q_i}/\text{bond}$	
			Primary	Secondary
$\text{C}_3\text{H}_8$	1.2	0.908	0.018	0.54
$\text{C}_3\text{H}_6\text{D}_2$	0.17	0.355	0.018	0.030

Although we do not feel that we are in a position to offer an exhaustive critique of sources of error in the work of Woodall and Gunning using nitric oxide, one possible difficulty is suggested by recent work of Holroyd and Pierce. The reported<sup>12</sup> that the Hg 1849 resonance radiation causes photosensitized decomposition of alkanes in a manner similar to that of the 2537 Å. radiation, except that  $k_5/k_4$  is approximately unity

for this process. The work<sup>2</sup> which led to the conclusion with which we disagree was performed using a quartz cell and quartz lamp which probably transmitted some, perhaps an appreciable amount, of the 1849 line. It is known<sup>18</sup> that the absorption coefficient for the 1849 line by mercury is much larger than for the 2537 line. If the mercury pressure and cell-absorption path length were small enough to cause incomplete absorption of the 2537 radiation, a large fraction of the decomposition may have been caused by the 1849 line. This would have resulted in the lower isopropyl- $n$ -propyl ratio reported in that work than we found using a Vycor lamp. Avrahami and Kebarle<sup>19</sup> have studied the mercury photosensitized decomposition of isotopically substituted propanes at low pressures and high light intensity. Under their conditions (typically 10 mm. of He, 5  $\mu$  of propane, 10% decomposition in 1.5 msec.) radical-radical reactions involving hydrogen atoms are very important. They estimated that over 40% of the primary decomposition reverted to propane through propyl radical-hydrogen atom recombination. Molecular hydrogen is produced via atom-radical disproportionation. Using simultaneous decomposition of  $\text{Hg}(\text{CD}_3)_2$ , they believed that they could obtain reliable estimates of  $n$ -propyl-isopropyl yields through measurements of the  $n$ -butane-isobutane product ratio. They obtained a value of 1.2 for  $k_5/k_4$ , in contrast to our value of 9.9. There are some difficulties, however, with their interpretations. The effects of the atomic hydrogen reactions in changing the propyl radical ratio are unknown. About 20% of the propylene, which supposedly arises only from  $\text{CD}_3 + \text{C}_3\text{H}_7$  disproportionation, recovered from runs using  $\text{Hg}(\text{CD}_3)_2 + \text{C}_3\text{H}_8$  was  $\text{C}_3\text{H}_5\text{D}$ . It seems perhaps unlikely that their high value of 0.5 for the disproportionation-recombination ratio of the propyl + methyl reaction can be explained by a hot radical effect persisting for  $10^4$  collisions with He and 5-10 collisions with propane. The fate or role of the hydrogen atoms was not considered in experiments with  $\text{Hg}(\text{CD}_3)_2$ . The butanes and propylene amounted at most to only 7.5% of the decomposition products. Thus we feel that these results are obtained from a reaction system which is sufficiently complicated to provide a number of ambiguities and a primary product ratio which we think is not well determined.

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