



Mechanism of Propane Formation by Ethane Photolysis at 1470 Å

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 $\eta_1 = -1769.7$, and $\eta_0 = 14017$. Figure 1 is the superposition of our results (broken curves) on Flory and Jernigan's (solid curves). Results for other n's are: *n*, $\langle r^2 \rangle / nb^2$ (Flory and Jernigan), $\langle r^2 \rangle / nb^2$ [Eq. (1)]: 263, 7.183, 7.1821; 519, 7.261, 7.2583; 1031, 7.300, 7.2972; 16391, 7.338, 7.3341. For $\langle r^4 \rangle / \langle r^2 \rangle^2$ with n =1027, they reported 1.65 but we obtain 1.6527. The small discrepancies observed for n larger than 1000 appear to be due to the possible difference in the values of σ used, not due to the inaccuracy of Eqs. (1) and (2). In view of the extreme smallness of the difference in the values of σ used, as judged from the close similarity of the values of ζ_1 obtained, the above comparison, though quite limited in amount, suggests that there is a considerable range of n where Eqs. (1) and (2) are sufficiently accurate while the deviation from the

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THERE have been several papers on the subject of \mathbf{L} ethane photolysis at 1470 Å¹⁻⁸ in which the mechanism of ethane photolysis has been discussed in detail. Until now, nothing has been reported about how propane is produced. Thus, we discuss the mechanism of propane formation at 1470 Å.

We carried out the photolysis of $C_2H_6+C_2D_4$ mixtures in which ethylene was about 1% of ethane to reduce the absorption of light by ethylene. Deuterated ethylene was added for the purpose of scavenging the hydrogen atoms produced in the primary process of ethane photolysis.

FIG. 1. $\langle r^2 \rangle / nb^2$ and $\langle r^4 \rangle / \langle r^2 \rangle^2$ of the polyethylene chain plotted against *n*, the number of C-C bonds. Solid lines: exact, Flory and Jernigan; broken lines: approximate, Nagai.

Gaussian behavior (i.e., the deviation of $\langle r^2 \rangle / nb^2$ from ζ_1 and of $\langle r^4 \rangle / \langle r^2 \rangle^2$ from 5/3) itself remains moderate.

* Read before the Joint U.S.-Japan Seminar in Polymer Physics, 18-23 October 1965, Kyoto, Japan.

¹K. Nagai, J. Chem. Phys. **38**, 924 (1963). Some expressions of this paper are in error. The revision will be made elsewhere, owing to lack of space. The present calculation is based on revised

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Two mechanisms were considered for propane formation. They are:

Mechanism 1. If propane is produced by the insertion into ethane of methylene formed in the primary process

$$C_2H_6 \xrightarrow{\mu\nu} CH_2 + CH_4, \qquad (1)$$

the propane formed would be only C_3H_8 .

Mechanism 2. Propane is produced by the reaction of methyl radicals and ethyl radicals formed by scavenging hydrogen atoms with ethylene. H atoms are formed in one of the primary processes of ethane photolysis.² Since a small amount of C₂D₄ absorbs the Xe resonance line, D atoms would also be produced in one of its primary processes. When these processes occur, H and D atoms are scavenged by C2H4 produced in one of the primary processes of ethane photolysis,² and by C_2D_4 to form ethyl radicals. Since the ethyl radicals formed in these processes are C_2H_5 , C₂H₄D, C₂D₄H, and C₂D₅, and methyl radicals are

No.	Pressure (mm)		Exposure	Propane (ratio)					
	C ₂ H ₆	C_2D_4	(min.)	do	<i>d</i> ₁	d_2, d_3	<i>d</i> 4	<i>d</i> ₆	d ₆ , d ₇ , d ₈
1	13.7	0.14	120	100	23	0	29	7	0
2	28.0	0.30	120	100	24	0	30	8	0
3	27.3	0.27	120	100	31	0	50	15	0

TABLE I. Isotopic distribution of propane produced in the photolysis of $C_2H_6+C_2D_4$ mixtures.

produced only from ethane to form CH₃, the propane produced should be d_{0} , d_1 , d_4 , and d_5 .⁴

Table I shows the approximate isotopic analysis of propanes formed in the photolysis of $C_2H_6+C_2D_4$ mixtures. Apparently, the experimental results are in good agreement with the presumption of the second mechanism. In this case, since the methyl radical is only CH₃, the isotopic ratio of the propane formed corresponds to that of ethyl radicals. Therefore, as the ratio of H/D is represented by C_2H_5/C_2H_4D and by C_2D_4H/C_2D_5 , the ratios of d_0/d_1 and d_4/d_5 of propane formed corresponds to H/D and these two values must agree with each other. Similarly, a ratio of C_2H_4/C_2D_4 is represented by d_0/d_4 and d_1/d_5 of propanes. These values are given in Table II and are in good agreement with each other. Therefore, it is concluded that formation of propane at low pressure is operated by Mechanism 2.

In order to clarify the mechanism of methyl formation in ethane photolysis, C_2H_6 and $C_2H_6+C_2H_4$ mixtures were used as samples.

Methyl radicals are produced by one of the primary processes,

$$C_2H_6 \rightarrow 2CH_3$$
 (2)

or by decomposition of excited propanes produced by the insertion reaction of methylene produced in Reaction (1) into ethane. Since there is high ethyl-radical concentration at high conversion, all methyl radicals produce propane through the combination reaction with ethyl radicals. Under this condition, for each ethane decompoased by Primary Process (2), two propanes and no methane are produced, whereas, for Primary Process (1), one propane and one methane are produced. Thus, the ratio of propane/methane indicates the relative weight of Process (2) and Process

TABLE II. The ratio of H/D and C_2H_4/C_2D_4 .

	\mathbf{H}_{i}	/D	C_2H_4/C_2D_4		
No.	d_0/d_1	d_4/d_5	d_0/d_4	d_1/d_s	
1	4.3	4.1	3.4	3.3	
2	4.2	3.8	3.3	3.0	
3	3.2	3.3	2.0	2.1	



FIG. 1. Time dependency of the propane/methane ratio. O, $C_2H_6(5.8 \text{ mm})$; \bigoplus , $C_2H_6(5.8 \text{ mm}) + C_2H_4(0.23 \text{ mm})$.

(1). The experimental results of this ratio versus exposure time are shown in Fig. 1. As the conversion becomes higher because of the stationary concentration of the ethyl radical, the ratio reaches a constant value of 1.8. Moreover, when a small amount of ethylene is added, the ratio is the same value even at low conversion. This is explained by the fact that the ethyl-radical concentration is stationary from the beginning under this condition. From the value of 1.8 it is calculated that the minor primary process (2) is about 0.7% of the total primary process using the value of 1.3° as a percentage of Primary Process (1).³

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⁸ R. F. Hampson, Jr., and J. R. McNesby, J. Chem. Phys. 42, 2200 (1965). ⁴ d₀, d₁, d₄, and d₅ mean C₃H₈, C₂H₇D, C₃H₄D₄, and C₃H₃D₅,

 ${}^{4}d_{0}$, d_{1} , d_{4} , and d_{5} mean C₃H₈, C₃H₇D, C₃H₄D₄, and C₃H₃D₅, respectively.

Comments

Comment on "On Derivations of the Uncertainty Principle"*

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I N a recent note¹ Davidson brings up an apparent paradox concerning the use of commutators, which he claims, displays a contradiction in the well-known^{2,3} general proof of the Heisenberg uncertainty relations. He further resolves this paradox by proposing the theorem that, if the commutator of Operators A and B is a *c*-number, then the class of functions over which they are Hermitian is restricted such that A is not

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