The Mercury-photosensitized Decomposition of Neopentane at High Temperatures

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The investigation of mercury-photosensitized reactions has been restricted mainly to simple hydrocarbons. Recent developments in gas chromatographic techniques have, however, made the study of the reactions of complex hydrocarbons feasible.

Darwent and Steacie1) have studied the mercury photosensitization of neopentane and have found that the main products at room temperature were hydrogen and dineopentyl. Methane was a minor product, and its formation was assumed to be due to atomic cracking. One of the characteristic features observed in their study of neopentane was that the quantum yield of hydrogen was extremely low and fairly temperature-dependent, the apparent activation energy being 4.3 kcal. The mercury photosensitization of methane also gives low quantum yields of hydrogen.2) It is possible that there is some correlation between the low quantum yield of hydrogen and the symmetry of the methane and neopentane molecules. Recently Back and van der Auwera3) have discussed the various possibilities in an attempt to explain this abnormality.

The mercury-photosensitized decomposition of most alkane molecules proceeds initially by the scission of the C–H bond. The radicals thus produced may combine together or may disproportionate at room temperature, while at high temperatures they decompose to smaller radicals and olefin molecules.4-6) Neopentyl radicals may be expected to behave similarly, with a rather low activation energy.

Experimental

Neopentane (supplied by Takachiho-Shoji Co.) was purified by bulb-to-bulb distillation, and the middle third was used for the photochemical studies. No impurities were detected by gas chromatographic analysis, indicating that the impurity content is at most below 0.1 %.

The quartz reaction cell (5 cm. wide internally, 8 cm. long) was placed in a furnace, the temperature of which was controlled by a thermister within ±1°C below 200°C and ±5°C above 250°C. A spiral mercury resonance lamp (filled with 4 mm. neon) illuminated the reaction cell through a quartz window of the furnace. The reaction cell was connected to the rest of the apparatus through a mercury cut-off.

After each run, the products were transferred to a trap at the liquid nitrogen temperature. The non-condensable gases (hydrogen and methane) were collected by a Toepler pump and the amount measured by a gas buret. The gas was passed over cuprous oxide at 250°C to remove hydrogen, and the amount of gas remaining was measured as methane. The condensable fraction was analyzed by gas chromatography. The column for the analysis of C_3 hydrocarbons and greater was packed with a Celite-dimethylsulpholane mixture (17 m. long) supplied by Shimadzu Co., and the column for the separation of ethane and ethylene was packed with a silica-squalane mixture (1 m. long).

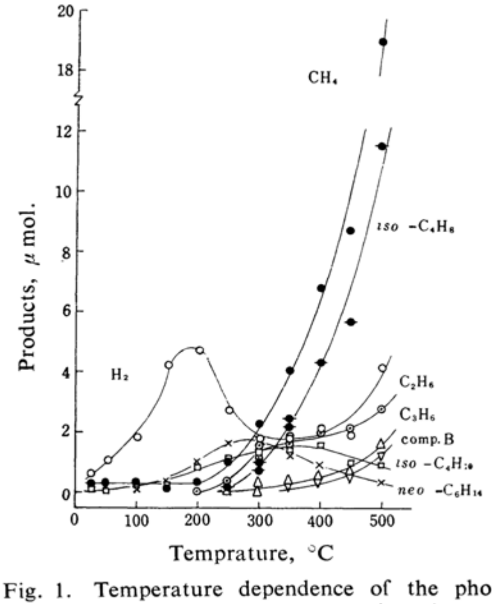

Fig. 1. Temperature dependence of the photosensitized reactions; Comp. B is unknown product, probably C_6.

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1) B. deB. Darwent and E. W. R. Steacie, *Can. J. Research*, 27, 181 (1949).

2) K. Morikawa, W. S. Benedict and H. S. Taylor, *J. Chem. Phys.*, 5, 212 (1937).

3) R. A. Back and D. van der Auwera, *Can. J. Chem.*, 40, 2339 (1962).

4) J. A. Kerr and A. F. Trotman-Dickenson, "Progress in Reaction Kinetics," Pergamon Press, London (1961), p. 105.

5) S. Arai, S. Sato and S. Shida, *J. Chem. Phys.*, 33, 1277 (1960).

6) S. Arai and S. Shida, *J. Chem. Soc. Japan, Ind. Chem. Sec.* (*Kogyo Kagaku Zasshi*), 64, 454 (1961).

TABLE I. PRESSURE DEPENDENCE OF THE FORMATION OF HYDROGEN AND METHANE*

Temperature ; 50°C						
Initial pressure, mmHg	12.2	22.0	36.4	51.2	81.4	164.2
Hydrogen, μmol.	0.52	0.78	1.20	1.40	2.30	2.79
Methane, μmol.	0.92	0.98	0.81	0.76	0.48	0.52
Temperature ; 100°C						
Initial pressure, mmHg	17.2	21.0	25.6	28.8	55.6	90.2
Hydrogen, μmol.	1.36**	1.85	2.12	2.22	3.30	4.81
Methane, μmol.		0.38	0.40	0.19	0.70	0.12
Temperature ; 150°C						
Initial pressure, mmHg	11.4	23.4	38.4	58.4	87.0	174.0
Hydrogen, μmol.	3.23	6.35	9.42	11.96	17.23	18.92
Methane, μmol.	0.65	0.52	0.41	0.38	0.28	0.34
Isobutane, μmol.	0.60	0.64	0.69			0.55
Neohexane, μmol.	0.56	0.47	0.48	0.56		0.23

* Reaction time ; 5 min.

** Mixture of hydrogen and methane

Results and Discussion

The Temperature Dependence of the Photosensitized Reaction.—In Fig. 1 the amounts of analyzed products from the mercury-photosensitized decomposition of neopentane are plotted as a function of the temperature. The initial neopentane pressure is 30 mmHg and the irradiation time is 5 min. in all cases. Below 250°C, the main products were hydrogen, isobutane, neohexane and methane, while propane was a minor product in all runs. The apparent activation energies for the rate of the formation of hydrogen (25°C to 150°C) and of isobutane and neohexane (25°C to 250°C) were calculated as 4.2 kcal. This value agrees with the activation energy of hydrogen formation obtained by Darwent and Steacie.[1]

Above 250°C, the amounts of methane, isobutene, ethane and propylene markedly increase with the increasing temperature. These products may arise from the decomposition of the neopentyl radicals produced initially. The apparent activation energies for the rates of the formation of methane, isobutene and propylene were 9 kcal. The amounts of isobutane and neohexane decreased with the increasing temperature above 250°C, possibly corresponding to the decomposition of neopentyl radicals. The curve for hydrogen is obviously abnormal. This will be discussed later.

Initial Process.—Table I shows the amounts of the main products from the mercury-photosensitized decomposition of neopentane at various initial pressures and at the temperatures of 50, 100 and 150°C. The ratios of the amounts of methane to those of hydrogen are plotted against the initial pressures in Fig. 2.

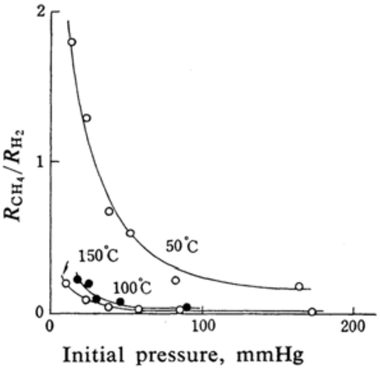

Fig. 2. Pressure dependence of the formations of hydrogen and methane.

To explain these results, the following mechanism is proposed for the formation of hydrogen and methane:

$$Hg + h\nu \rightarrow Hg^{*}\ (^3P_1)$$

$$Hg^{*} \rightarrow Hg + h\nu \qquad (1)$$

$$Hg^{*} + neo\text{-}C_5H_{12} \begin{cases} \rightarrow Hg + neo\text{-}C_5H_{12} & (2) \\ \rightarrow Hg + neo\text{-}C_5H_{11} + H & (3) \end{cases}$$

$$H + neo\text{-}C_5H_{12} \rightarrow H_2 + neo\text{-}C_5H_{11} \qquad (4)$$

$$H + neo\text{-}C_5H_{11} \rightarrow CH_3 + t\text{-}C_4H_9 \qquad (5)$$

$$CH_3 + neo\text{-}C_5H_{12} \rightarrow CH_4 + neo\text{-}C_5H_{11} \qquad (6)$$

Here, reaction 2 refers to the physical quenching of the excited mercury atom by the neopentane molecule. This reaction is considered to take part in the mechanism because the quantum yield of hydrogen is known to be extremely low in the mercury-photosensitized reaction of neopentane.[1] Reaction 5 is atomic cracking of neopentyl radicals by hydrogen atoms.[7] The steady-state treatment of

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[7] E. W. R. Steacie, "Atomic and Free Radical Reaction," Reinhold Publishing Co., New York (1946).

the above mechanism gives the following relation:

$$\frac{I}{R_{\text{non}}}=\frac{k_2+k_3}{k_3}\left\{1+\frac{k_1}{(k_2+k_3)\,[\mathrm{C_5H_{12}}]}\right\} \qquad \text{(I)}$$

where I is the intensity of light, R_{non} is the rate of the formation of non-condensables, and k_1 is the reciprocal of the life-time of the excited mercury atom ($\tau=1.08\times10^{-7}$ sec.). Using the data from Table I, a linear correlation between the reciprocal of the rate of the formation of non-condensables and the reciprocal of the initial neopentane pressure is obtained (see Fig. 3). The values of k_2+k_3 calculated from the slope and intercept are given in Table II. In Fig. 3, data obtained at low pressures are scattered, probably due to the importance of the recombination of methyl radicals and wall effects. Therefore, the scattered data have not been used for the calculations of k_2+k_3 in Table II.

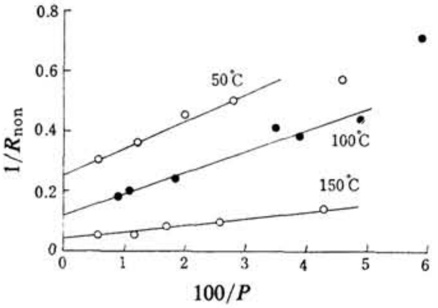

Fig. 3. Reciprocal of the rate of formation of non-condensables as a function of reciprocal of the initial pressure.

TABLE II. QUENCHING CROSS SECTIONS OF THE NEOPENTANE MOLECULE

	50°C	100°C	150°C
k_2+k_3 (l. mol^{-1} sec^{-1})	4.3×10^9	4.4×10^9	5.3×10^9
$\sigma_{\mathrm{C_5H_{12}}}$ (Å^2)	0.63	0.60	0.68

The calculated values of k_2+k_3 are almost temperature independent. From these values, the mean quenching cross section of neopentane for excited mercury atoms is calculated as 0.64 Å^2, which is smaller than one-half of the value obtained photometrically by Darwent.[8] In the previous section, 4.2 kcal. was obtained for the apparent activation energy of hydrogen formation. This can be explained from Eq. I if $k_2 \gg k_3$ and $E_3 \simeq 4$ kcal. However, the reason for the high activation energy of reaction 3 cannot be explained from the findings of the present work. The same problem has been encountered by Back and van der Auwera for methane.[3]

Atomic Cracking. — Most of the neopentyl radicals produced may combine with each other to give dineopentyl at low temperatures, i. e.,

$$2\ \mathrm{C_5H_{11}} \rightarrow \mathrm{C_{10}H_{22}} \qquad (7)$$

When neopentane pressure is high, R_4 would be much greater than R_5 and, thus, the steady state treatment would give the following equation:

$$R_{\mathrm{CH_4}}{}^2/R_{\mathrm{H_2}}{}^3=k_5{}^2/k_4{}^2k_7\,[\mathrm{C_5H_{12}}]^2 \qquad \text{(II)}$$

where $R_{\mathrm{CH_4}}$ and $R_{\mathrm{H_2}}$ are the rates of the formation of methane and hydrogen respectively. If it is assumed that reactions 5 and 7 have no or very little activation energy and that reaction 4 has an activation energy of several killocalories,[4] the values of $R_{\mathrm{CH_4}}/R_{\mathrm{H_2}}$ at high pressures are consistent with Eq. II (see Fig. 2).

Below 150°C, small amounts of propane have always been found by gas chromatography and may arise from the atomic cracking of the tert-butyl radicals produced by reaction 5:

$$\mathrm{H} + t\text{-}\mathrm{C_4H_9} \rightarrow \mathrm{CH_3} + \mathrm{C_3H_7} \qquad (8)$$

$$\mathrm{C_3H_7} + \mathrm{C_5H_{12}} \rightarrow \mathrm{C_3H_8} + \mathrm{C_5H_{11}} \qquad (9)$$

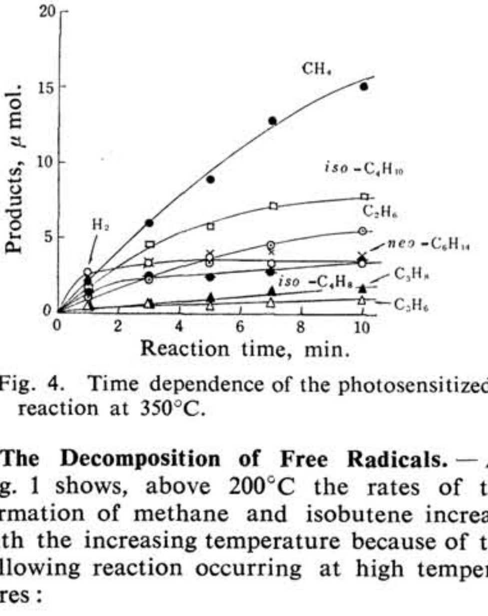

Fig. 4. Time dependence of the photosensitized reaction at 350°C.

The Decomposition of Free Radicals. — As Fig. 1 shows, above 200°C the rates of the formation of methane and isobutene increase with the increasing temperature because of the following reaction occurring at high temperatures:

$$neo\text{-}\mathrm{C_5H_{11}} \rightarrow \mathrm{CH_3} + i\text{-}\mathrm{C_4H_8} \qquad (10)$$

The methyl radicals produced in reaction 10 may abstract hydrogen atoms from neopentane molecules and give neopentyl radicals, which may again undergo reaction 10, so that metane and isobutene are produced by a chain mechanism.

Table III and Fig. 4 show the time dependence on the reaction products. The amounts of hydrogen and isobutene are not linear with the irradiation time up to one minute below

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[8] B. deB. Darwent, *J. Chem. Phys.*, **18**, 1532 (1950).

TABLE III. TIME DEPENDENCE OF THE PHOTOCHEMICAL REACTION AT HIGHER TEMPERATURES

Temp. °C	Initial pressure mmHg	Reaction time min.	Products, μ mol.							
			H_2	CH_4	C_2H_6	C_3H_8	C_3H_6	i-C_4H_{10}	i-C_4H_8	neo-C_6H_{14}
250	32.0	1	3.40	0.36						
	30.8	1	3.10	0.36				0.55		0.94
300	32.4	1/2	1.26	0.67	0.18	0.16	0.09	0.51	0.28	0.80
	30.0	1	2.23	1.52	0.46	0.14	0.05	1.70	0.92	1.08
	30.0	3/2	2.41	2.28	0.69	0.18	0.08	1.75	0.46	2.02
400	30.2	1/2	1.40	1.26	0.87	0.07	0.10	2.08	1.94	0.68
	30.8	1	1.55	2.68	1.47*		0.23	1.56	3.08	1.68
465	30.4	1/4	0.79	1.84	0.78		0.16	0.23	3.29	0.32
500	31.0	35 dark	(0.91)						0.37	
	31.6	1/6	0.94	2.12	0.76		0.01	0.18	4.41	0.24
	30.4	1/2	1.85	3.97	1.47	0.09	0.32	0.50	5.61	0.28
	30.4	1	2.41	5.78	2.32**	0.21	0.62	1.06	6.05	0.54

* C_2H_6 1.33 μ mol., C_2H_4 0.14 μ mol.
** C_2H_6 2.11 μ mol., C_2H_4 0.21 μ mol.

300°C, while methane increases linearly even at 400°C. This may be explained by the combination of two effects; hydrogen has a much larger quenching cross section for the excited mercury atom than does methane ($\delta_{H_2}=8.60\,\text{Å}^2$, $\sigma_{CH_4}=0.085\,\text{Å}^2$)9), and isobutene is reactive to radicals; for example:

$$H + i\text{-}C_4H_8 \rightarrow t\text{-}C_4H_9 \qquad (11)$$

On the basis of these discussions, the abnormality of the curve for hydrogen in Fig. 1 may be understood. In fact, the initial rates of the formation of hydrogen do not show any abnormality (see Table III). At 500°C, however, the amount of hydrogen increases markedly. A possible explanation is that the scission of the C–H of radicals is occurring at higher temperatures,4) for example,

$$t\text{-}C_4H_9 \rightarrow i\text{-}C_4H_8 + H \qquad (12)$$

Figure 5 shows the relationship between the logarithm of the initial rates of the formation of methane and isobutene and the reciprocal of the temperature. Values for the logarithm of the initial rate of methane formation are not linear at low temperatures, since small amounts of methane produced by atomic cracking. At high temperatures, the amout of methane is a little less than that of isobutene, probably because methane is not an only product from the methyl radical.

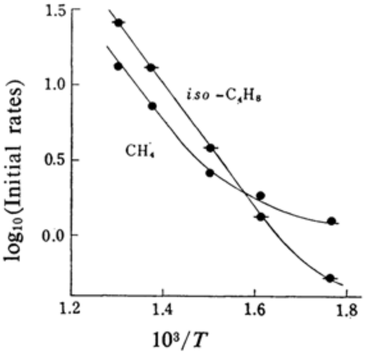

Fig. 5. Logarithm of initial rate of formation as a function of reciprocal of temperature.

These results may reasonably be explained by the following mechanism:

$$H + C_5H_{12} \rightarrow H_2 + C_5H_{11} \qquad (4)$$

$$C_5H_{11} \rightarrow CH_3 + i\text{-}C_4H_8 \qquad (10)$$

$$CH_3 + C_5H_{12} \rightarrow CH_4 + C_5H_{11} \qquad (6)$$

$$C_5H_{11} + C_5H_{11} \rightarrow C_{10}H_{22} \qquad (7)$$

$$CH_3 + C_5H_{11} \rightarrow C_6H_{14} \qquad (13)$$

$$CH_3 + CH_3 \rightarrow C_2H_6 \qquad (14)$$

When the temperature is not too high, it may be assumed that $R_7 \gg R_{13}$, because the concetration of the methyl radical is much lower than that of the neopentyl radical. Therefore the steady-state treatment gives the following relation:

$$R_{CH_4}/\sqrt{R_{H_2}} \simeq R_{C_4H_8}/\sqrt{R_{H_2}} = k_{10}/\sqrt{k_7} \qquad \text{(III)}$$

$R_{C_4H_8}$ and R_{H_2} are calculated from Table III using the data at short irradiation times. Figure 6 shows the straight relationship between the logarithm of $R_{C_4H_8}/\sqrt{R_{H_2}}$ and the reciprocal of the temperature. From the slope of this line,

$$E_{10} - 1/2E_7 = 15.0\,\text{kcal.}$$

Since the activation energy of reaction 7 can be assumed to be about zero to 4 kcal., 17 ±2 kcal. is obtained for the activation energy of reaction 10. This value is reasonable when compared to the activation energy of hydrocarbon radical decomposition.4)

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9) K. J. Laidler, "The Chemical Kinetics of Excited States," Clarendon Press., London (1955), p. 107.

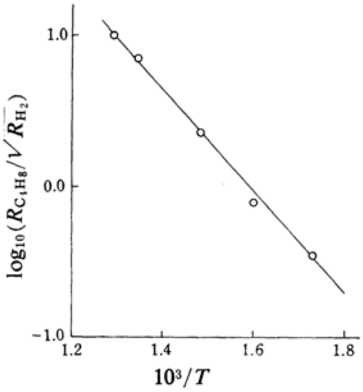

Fig. 6. Activation energy of decomposition of neopentyl radical.

The propylene observed at higher temperatures may be due to the decomposition of the butyl radical, as follows:

$$t\text{-}C_4H_9 \rightarrow i\text{-}C_4H_9 \rightarrow CH_3 + C_3H_6 \qquad (15)$$

However, no quantitative treatment has been attempted, because the amount of propylene produced is small and many speculations have to be made for the isomerization of radicals, although much information has recently been accumulated.[10]

Summary

The mercury-photosensitized decomposition of neopentane has been investigated over the temperature range 25°C to 500°C. If the quenching of excited mercury atoms by neopentane molecules is assumed to occur both physically and chemically, as follows:

$$Hg^{*+}(^3P_1) + neo\text{-}C_5H_{12} - \begin{cases} \rightarrow Hg + neo\text{-}C_5H_{12} & (2) \\ \rightarrow Hg + C_5H_{11} + H & (3) \end{cases}$$

it has been shown that $k_2 \gg k_3$ and that the quenching cross section of reaction is about 0.6 Å^2, which is almost temperature independent, and $E_3 \simeq 4$ kcal. Above 250°C, neopentyl radicals decompose to methyl radicals and isobutene molecules with an activation energy of 17 ± 2 kcal.

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[10] J. R. McNesby and W. M. Jackson, *J. Chem. Phys.*, **38**, 692 (1963).